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MECHANICS

LIMITING STRESSES OF A CRUMBLING AND EARTHY LAMELLAR MEDIUM

By V. SOKOLOVSKY

(Communicated by N. E. Kotchin, Member of the Academy, 27. VI. 1939)

This paper contains a generalization of our theory of limiting equilibrium of a crumbling and earthy medium (1).

Now we shall consider a medium where the angle of friction $\bar{\rho}$ and the coefficient of cohesion $\frac{\bar{K}}{\cos\bar{\rho}}$ along horizontal planes * will be less than the corresponding angle of friction ρ and the cohesion coefficient $\frac{K}{\cos\rho}$ along other planes **:

$$\bar{\rho} < \rho, \quad \frac{\bar{K}}{\cos\bar{\rho}} < \frac{K}{\cos\rho}.$$

At each point of such a medium besides the condition

$$|\tau_{nt}| \leqslant \frac{K}{\cos\rho} + \sigma_n \operatorname{tg}\rho, \tag{1}$$

the condition

$$|\tau_{xy}| \leqslant \frac{\bar{K}}{\cos\bar{\rho}} + \sigma_x \operatorname{tg}\bar{\rho} \tag{2}$$

must be satisfied. Thus, when a limiting state occurs, we shall have in this problem two regions, in one of which

$$|\tau_{nt}| = \frac{K}{\cos\rho} + \sigma_n \operatorname{tg}\rho, \quad |\tau_{xy}| \leqslant \frac{\bar{K}}{\cos\bar{\rho}} + \sigma_x \operatorname{tg}\bar{\rho} \tag{3}$$

and in the other

$$|\tau_{nt}| \leqslant \frac{K}{\cos\rho} + \sigma_n \operatorname{tg}\rho, \quad |\tau_{xy}| = \frac{\bar{K}}{\cos\bar{\rho}} + \sigma_x \operatorname{tg}\bar{\rho}. \tag{4}$$

These regions are separated by curves, along which

$$|\tau_{nt}| = \frac{K}{\cos\rho} + \sigma_n \operatorname{tg}\rho, \quad |\tau_{xy}| = \frac{\bar{K}}{\cos\bar{\rho}} + \sigma_x \operatorname{tg}\bar{\rho}. \tag{5}$$

* It is easy to apply the same reasonings to the case when the planes of the layers are inclined.

** We shall assume that $K\sin\bar{\rho} \geqslant \bar{K}\sin\rho$ which is usually the case, because $\bar{K}$ is small.

The formulae (3), (4), (5) may respectively be re-written as follows:

$$\sqrt{\left(\frac{\sigma_x-\sigma_y}{2}\right)^2+\tau_{xy}^2}-\sin\rho\frac{\sigma_x+\sigma_y}{2}=K,\ |\tau_{xy}|\leqslant\frac{\bar{K}}{\cos\bar{\rho}}+\sigma_x\operatorname{tg}\bar{\rho} \tag{3'}$$

$$\sqrt{\left(\frac{\sigma_x-\sigma_y}{2}\right)^2+\tau_{xy}^2}-\sin\rho\frac{\sigma_x+\sigma_y}{2}\leqslant K,\ |\tau_{xy}|=\frac{\bar{K}}{\cos\bar{\rho}}+\sigma_x\operatorname{tg}\bar{\rho} \tag{4'}$$

$$\sqrt{\left(\frac{\sigma_x-\sigma_y}{2}\right)^2+\tau_{xy}^2}-\sin\rho\frac{\sigma_x+\sigma_y}{2}=K,\ |\tau_{xy}|=\frac{\bar{K}}{\cos\bar{\rho}}+\sigma_x\operatorname{tg}\bar{\rho}. \tag{5'}$$

In the paper [1] we assumed that

$$\left.\begin{aligned}\sigma_x&=\sigma[1+\sin\rho\sin(2\varphi+\rho)]-\frac{K}{\sin\rho}\\ \sigma_y&=\sigma[1-\sin\rho\sin(2\varphi+\rho)]-\frac{K}{\sin\rho},\quad \tau_{xy}=-\sigma\sin\rho\cos(2\varphi+\rho)\end{aligned}\right\}. \tag{6}$$

Substituting (6) in (3'), we obtain the values of φ corresponding to conditions (3):

$$\frac{\pi}{4}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}-\frac{\bar{\varkappa}}{2}\leqslant\varphi\leqslant\frac{\pi}{4}-\frac{\rho}{2}+\frac{\bar{\rho}}{2}+\frac{\bar{\varkappa}}{2} \tag{7'}$$

$$-\frac{\pi}{4}-\frac{\rho}{2}+\frac{\bar{\rho}}{2}-\frac{\bar{\varkappa}}{2}\leqslant\varphi\leqslant-\frac{\pi}{4}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}+\frac{\bar{\varkappa}}{2} \tag{7''}$$

where

$$\bar{\varkappa}=\arcsin\left(\frac{\sin\bar{\rho}}{\sin\rho}-\frac{K\sin\bar{\rho}-\bar{K}\sin\rho}{\sigma\sin^2\rho}\right).$$

Substituting (6) in (5'), we obtain the equations of curves, along which the conditions (5) are satisfied:

$$\sigma=\frac{K\sin\bar{\rho}-\bar{K}\sin\rho}{\sin\rho[\sin\bar{\rho}-\sin\rho\cos(2\varphi+\rho+\bar{\rho})]} \tag{8}$$

$$\sigma=\frac{K\sin\bar{\rho}-\bar{K}\sin\rho}{\sin\rho[\sin\bar{\rho}+\sin\rho\cos(2\varphi+\rho-\bar{\rho})]}. \tag{9}$$

In our paper [1] we adopted the following notation

$$\xi=\frac{\operatorname{ctg}\rho}{2}\ln\sigma+\varphi,\quad \eta=\frac{\operatorname{ctg}\rho}{2}\ln\sigma-\varphi. \tag{10}$$

Substituting (8) in (10), we obtain a curve having two branches. One branch of this curve

$$\left.\begin{aligned}&\xi=\xi_{II}(\varphi),\ \eta=\eta_{II}(\varphi)\quad\text{or}\quad \eta=F_{II}(\xi),\quad \varphi=\varphi_{II}(\xi),\quad \varphi=\varphi_{II}^{*}(\eta)\\ &\text{is obtained when } \varphi \text{ varies within the limits}\\ &\frac{\pi}{4}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}-\frac{1}{2}\arcsin\frac{\sin\rho}{\sin\bar{\rho}}\leqslant\varphi\leqslant\frac{\pi}{2}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}\end{aligned}\right\}. \tag{11'}$$

It is represented by BE in Fig. 1. The second branch of this curve

$$\left.\begin{aligned}&\xi=\xi_{III}(\varphi),\quad \eta=\eta_{III}(\varphi)\quad\text{or}\quad \eta=F_{III}(\xi),\quad \varphi=\varphi_{III}(\xi),\quad \varphi=\varphi_{III}^{*}(\eta)\\ &\text{is obtained when } \varphi \text{ varies within the limits}\\ &-\frac{\pi}{2}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}\leqslant\varphi\leqslant-\frac{\pi}{4}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}+\frac{1}{2}\arcsin\frac{\sin\rho}{\sin\bar{\rho}}\end{aligned}\right\}. \tag{11''}$$

It is represented by CL in Fig. 1.

Substituting (9) in (10), we obtain a curve consisting of two branches. One branch of this curve

$$\left.\begin{aligned} &\xi=\xi_{\mathrm{I}}(\varphi), \quad \eta=\eta_{\mathrm{I}}(\varphi) \quad \text{or} \quad \eta=F_{\mathrm{I}}(\xi) \\ &\text{is obtained when } \varphi \text{ varies within the limits} \\ &-\frac{\rho}{2}+\frac{\bar{\rho}}{2} \leqslant \varphi \leqslant \frac{\pi}{4}-\frac{\rho}{2}+\frac{\bar{\rho}}{2}+\frac{1}{2}\arcsin\frac{\sin\bar{\rho}}{\sin\rho} \end{aligned}\right\}. \qquad (12')$$

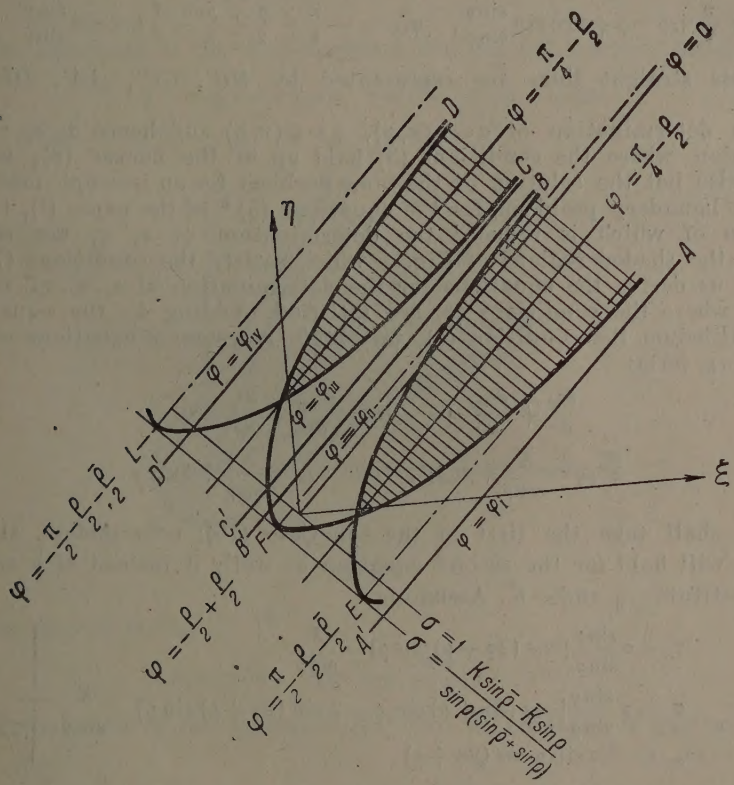

Fig. 1.

It is represented by AF in Fig. 1. The second branch of this curve

$$\left.\begin{aligned} &\xi=\xi_{\mathrm{IV}}(\varphi), \quad \eta=\eta_{\mathrm{IV}}(\varphi) \quad \text{or} \quad \eta=F_{\mathrm{IV}}(\xi) \\ &\text{is obtained when } \varphi \text{ varies within the limits} \\ &-\frac{\pi}{4}-\frac{\rho}{2}+\frac{\bar{\rho}}{2}-\frac{1}{2}\arcsin\frac{\sin\bar{\rho}}{\sin\rho} \leqslant \varphi \leqslant -\frac{\rho}{2}+\frac{\bar{\rho}}{2} \end{aligned}\right\}. \qquad (12'')$$

It is represented by DF in Fig. 1.

If we consider a crumbling medium ($K=\bar{K}=0$), then instead of (11), (12) on the plane (ξ, η) we shall obtain the following four straight lines respectively:

$$\eta=\xi-\frac{\pi}{2}+\rho+\bar{\rho}+\arcsin\frac{\sin\bar{\rho}}{\sin\rho}, \quad \varphi_{II}=\frac{\pi}{4}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}-\frac{1}{2}\arcsin\frac{\sin\bar{\rho}}{\sin\rho} \tag{13'}$$

$$\eta=\xi+\frac{\pi}{2}+\rho+\bar{\rho}-\arcsin\frac{\sin\bar{\rho}}{\sin\rho}, \quad \varphi_{III}=-\frac{\pi}{4}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}+\frac{1}{2}\arcsin\frac{\sin\rho}{\sin\rho} \tag{13''}$$

$$\eta=\xi-\frac{\pi}{2}+\rho-\bar{\rho}-\arcsin\frac{\sin\bar{\rho}}{\sin\rho}, \quad \varphi_{I}=\frac{\pi}{4}-\frac{\rho}{2}+\frac{\bar{\rho}}{2}+\frac{1}{2}\arcsin\frac{\sin\bar{\rho}}{\sin\rho} \tag{14'}$$

$$\eta=\xi+\frac{\pi}{2}+\rho-\bar{\rho}+\arcsin\frac{\sin\bar{\rho}}{\sin\rho}, \quad \varphi_{IV}=-\frac{\pi}{4}-\frac{\rho}{2}+\frac{\bar{\rho}}{2}-\frac{1}{2}\arcsin\frac{\sin\bar{\rho}}{\sin\rho} \tag{14''}$$

These straight lines are represented by BB', CC', AA', DD' in Fig. 1.

The determination of $\sigma=\sigma(x,y)$, $\varphi=\varphi(x,y)$ and hence $\sigma_x, \sigma_y, \tau_{xy}$ in the region where the conditions (3) hold up to the curves (8), is nothing else but the solution of the same problem for an isotropic medium.

The boundary problems for the equations (5)* of the paper [1], to the solution of which is reduced the determination of σ, φ, are solved within the shaded regions of Fig. 1 which satisfy the conditions (7).

Let us derive the equations for the determination of $\sigma_x, \sigma_y, \tau_{xy}$ in the region where the conditions (4) are satisfied. Adding to the equations of equilibrium the condition (4), we obtain a system of equations of the following form:

$$\frac{\partial\sigma_x}{\partial x}+\frac{\partial\tau_{xy}}{\partial y}+\gamma=0, \quad \frac{\partial\tau_{xy}}{\partial x}+\frac{\partial\sigma_y}{\partial y}=0 \tag{15}$$

$$-\tau_{xy}=\frac{\bar{K}}{\cos\rho}+\sigma_x\operatorname{tg}\bar{\rho} \quad \text{or} \quad \tau_{xy}=\frac{\bar{K}}{\cos\rho}+\sigma_x\operatorname{tg}\bar{\rho}. \tag{16}$$

We shall take the first of the equations (16); nevertheless, all the results will hold for the second equation as well, if instead of $\bar{\rho}$ and $\bar{K}$ we substitute $-\bar{\rho}$ and $-\bar{K}$. Assuming

$$\left.\begin{aligned}
\sigma_x&=\sigma\frac{\sin\rho}{\sin\bar{\rho}}[\cos(2\varphi+\rho)\cos\bar{\rho}]-\frac{\bar{K}}{\sin\rho}\\
\sigma_y&=\sigma\frac{\sin\rho}{\sin\bar{\rho}}[\cos(2\varphi+\rho)\cos\bar{\rho}-2\sin(2\varphi+\rho)\sin\bar{\rho}]-\frac{\bar{K}}{\sin\bar{\rho}}\\
\tau_{xy}&=-\sigma\sin\rho\cos(2\varphi+\rho)
\end{aligned}\right\} \tag{17}$$

and substituting (17) in (15), we obtain

$$\left.\begin{aligned}
&\frac{\partial\sigma}{\partial x}\cos(2\varphi+\rho)\cos\bar{\rho}-\frac{\partial\sigma}{\partial y}\cos(2\varphi+\rho)\sin\bar{\rho}-2\sigma\sin(2\varphi+\rho)\cos\bar{\rho}\frac{\partial\varphi}{\partial x}+\\
&\qquad+2\sigma\sin(2\varphi+\rho)\sin\bar{\rho}\frac{\partial\varphi}{\partial y}+\frac{\sin\bar{\rho}}{\sin\rho}\gamma=0\\
&\frac{\partial\sigma}{\partial y}\cos(2\varphi+\rho+2\bar{\rho})-2\sigma\sin(2\varphi+\rho+2\bar{\rho})\frac{\partial\varphi}{\partial y}+\frac{\sin^2\bar{\rho}}{\sin\rho}\gamma=0
\end{aligned}\right\} \tag{18}$$

We shall introduce the following abbreviations:

$$\bar{\xi}=\sigma\cos(2\varphi+\rho), \quad \bar{\eta}=\sigma\cos(2\varphi+\rho+2\bar{\rho}). \tag{19}$$

---

* It is easier to obtain the solution of the boundary problems for the equations (8) of the paper [1].

Substituting (19) in (17) and (18), we obtain

$$\left.\begin{aligned} \sigma_x &= \frac{\sin\rho}{\sin\bar{\rho}}\cos\bar{\rho}\,\bar{\xi} - \frac{\bar{K}}{\sin\rho} \\ \sigma_y &= \frac{\sin\rho}{\sin\bar{\rho}}\frac{1}{\cos\rho}[\bar{\xi}\sin^2\bar{\rho} - \bar{\eta}] - \frac{\bar{K}}{\sin\rho} \\ \tau_{xy} &= -\sin\rho\,\bar{\xi} \end{aligned}\right\} \tag{20}$$

$$\left.\begin{aligned} &\frac{\partial\bar{\xi}}{\partial x}\cos\bar{\rho} - \frac{\partial\bar{\xi}}{\partial y}\sin\rho + \frac{\sin\bar{\rho}}{\sin\rho}\gamma = 0 \\ &\frac{\partial\bar{\eta}}{\partial y} + \frac{\sin^2\bar{\rho}}{\sin\rho}\gamma = 0 \end{aligned}\right\} \tag{21}$$

The equations of the characteristics will be: for the first family

$$y + x\,\mathrm{tg}\,\bar{\rho} = \mathrm{const}, \quad \bar{\alpha} \equiv \bar{\xi} - \frac{\gamma}{\sin\rho}y = \mathrm{const} \tag{22'}$$

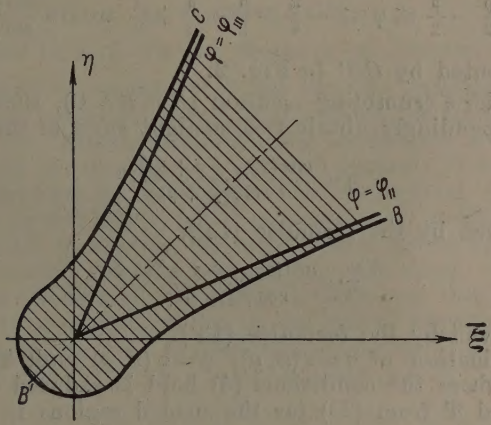

Fig. 2.

for the second family

$$x = \mathrm{const}, \quad \bar{\beta} \equiv \bar{\eta} + \frac{\sin^2\bar{\rho}}{\sin\rho}\gamma y = \mathrm{const}. \tag{22''}$$

The solution of the equations (21) will be obtained in the following form:

$$\left.\begin{aligned} &\bar{\xi} = \frac{\gamma}{\sin\rho}y + \bar{\alpha}, \quad \bar{\eta} = -\frac{\sin^2\bar{\rho}}{\sin\rho}\gamma y + \bar{\beta} \\ &y + x\,\mathrm{tg}\,\bar{\rho} = \Phi(\bar{\alpha}), \quad x = \Psi(\bar{\beta}) \end{aligned}\right\} \tag{23}$$

where Φ and Ψ are arbitrary functions.

In the absence of mass forces the solution of the equations will be

$$y + x\,\mathrm{tg}\,\bar{\rho} = \Phi(\bar{\xi}), \quad x = \Psi(\bar{\eta}) \tag{24}$$

where Φ and Ψ are arbitrary functions.

Substituting (17) in (4), we obtain the value of φ corresponding to the conditions (4):

$$-\frac{\pi}{4} - \frac{\rho}{2} - \frac{\bar{\rho}}{2} + \frac{\bar{\varkappa}}{2} \leqslant \varphi \leqslant \frac{\pi}{4} - \frac{\rho}{2} - \frac{\rho}{2} - \frac{\varkappa}{2}.$$

Substituting (17) in (5), we obtain the equations of the curve, along which hold the conditions in the form (8).

Substituting (8) in (19), we obtain a curve consisting of two branches. One branch of this curve

$$\left.\begin{aligned} &\bar{\xi}=\bar{\xi}_{II}(\varphi),\quad \bar{\eta}=\bar{\eta}_{II}(\varphi) \quad \text{or} \quad \bar{\eta}=\bar{F}_{II}(\bar{\xi}),\quad \varphi=\bar{\varphi}_{II}(\bar{\xi}),\quad \varphi=\bar{\varphi}^{*}_{II}(\bar{\eta}) \\ &\text{is obtained when } \varphi \text{ varies within the limits} \\ &\frac{\pi}{4}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}-\frac{1}{2}\arcsin\frac{\sin\bar{\rho}}{\sin\rho}\leqslant\varphi\leqslant\frac{\pi}{2}-\frac{\rho}{2}-\frac{\bar{\rho}}{2} \end{aligned}\right\} \quad (25')$$

It is represented by BB' in Fig. 2. The second branch of this curve

$$\left.\begin{aligned} &\bar{\xi}=\bar{\xi}_{III}(\varphi),\quad \bar{\eta}=\bar{\eta}_{III}(\varphi) \quad \text{or} \quad \bar{\eta}=\bar{F}_{III}(\bar{\xi}),\quad \varphi=\bar{\varphi}_{III}(\bar{\xi}),\quad \varphi=\bar{\varphi}^{*}_{III}(\bar{\eta}) \\ &\text{will be obtained when } \varphi \text{ varies within the limits} \\ &-\frac{\pi}{2}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}\leqslant\varphi\leqslant-\frac{\pi}{4}-\frac{\rho}{2}-\frac{\bar{\rho}}{2}+\frac{1}{2}\arcsin\frac{\sin\bar{\rho}}{\sin\rho} \end{aligned}\right\} \quad (25'')$$

It is represented by CB' in Fig. 2.

If we consider a crumbling medium ($K=\bar{K}=0$), then instead of (25) we shall correspondingly obtain two straight lines of the form

$$\bar{\eta}=\frac{\cos(2\varphi_{II}+\rho+2\bar{\rho})}{\cos(2\varphi_{II}+\rho)}\bar{\xi} \quad (26')$$

where φ_{II} is given by the formulae (13′),

$$\bar{\eta}=\frac{\cos(2\varphi_{III}+\rho+2\bar{\rho})}{\cos(2\varphi_{III}+\rho)}\bar{\xi} \quad (26'')$$

where φ_{III} is given by the formulae (13″).

The determination of $\sigma=\sigma(x,y)$, $\varphi=\varphi(x,y)$ and, hence, σ_x, σ_y, τ_{xy} in the region where the conditions (4) hold is reduced to the determination of Φ and Ψ from (23) for the shaded regions in Fig. 2.

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MECHANICS

GENERALIZED PRANDTL PROBLEM FOR A LAMELLAR EARTHY MEDIUM

By V. SOKOLOVSKY

(Communicated by N. E. Kotchin, Member of the Academy, 27. VI. 1939)

In(1) we extended the theory of the limiting equilibrium to the case of a medium with horizontal layers, along which the friction and cohesion coefficients are less than the corresponding coefficients in other directions.

Below is given the solution of a problem formerly(2) denoted as a generalized Prandtl problem for such a type of earthy medium. Along the portion AB is given the normal load $\sigma_x(y)$; it is necessary to find the minimum normal load along AN preventing the protrusion of the earth within this portion. Let us consider the case when along AB $\sigma'_x(y) > 0$, corresponding to a monotonous increase of load along the axis y at this portion.

First let us analyze the problem in the case of absence of the mass forces. Let us introduce into the analysis two planes: (ξ, η) and $(\bar{\xi}, \bar{\eta})$, it being known that the plane (ξ, η) is a many-sheeted one.

On the first sheet of the plane (ξ, η) let us draw $\eta = \xi - \frac{\pi}{2} + \rho$, where the portion ab corresponds to the region of load AB. In the triangle abc on the upper sheet we solve the Cauchy problem for the equations (5) of(1), as it was the case in(1). Let us join the both sheets along ac. On the second sheet we draw the curve (12') of(1). The points of intersection of this curve with the characteristics $\eta = \text{const}$, passing through a and b will be denoted as d and f. To the portion of the characteristic ad corresponds the point A on the plane (x, y) with co-ordinates $(0, 0)$. Therefore along ad let us assume $x = 0$, $y = 0$.

Solving Goursat's problem for the equations (5) of(1) we determine x, y in the rectangle $adec$ as it has been done in(1). We will obtain $x = x(\eta)$, $y = y(\eta)$ along the portion of the characteristic de.

Using the formulae* (11'), we find φ for the points d and f

$$\varphi_d = \varphi^*_{II}(\eta_a), \quad \varphi_f = \varphi^*_{II}(\eta_b).$$

On the plane $(\bar{\xi}, \bar{\eta})$ let us draw the curves (25') and (25''); substituting φ_d and φ_f in (25') we obtain the points $\bar{d}$ and $\bar{f}$. The points of intersection of the curve (25'') with the characteristics $\bar{\eta} = \text{const}$ passing through $\bar{d}$ and $\bar{f}$ will be denoted as $\bar{g}$ and $\bar{i}$ (Fig. 1, c).

---

* The formulae denoted by numbers are to be found in (1).

Using the formulae (25″), we find φ for the points $\bar{g}$ and $\bar{i}$:

$$\varphi_{\bar{g}} = \bar{\varphi}^{*}_{\mathrm{III}}(\bar{\eta}_{\bar{d}}), \quad \varphi_{\bar{i}} = \bar{\varphi}^{*}_{\mathrm{III}}(\bar{\eta}_{\bar{f}}).$$

On the third sheet of the plane (ξ, η) let us draw the curve (11″) and the straight line $\eta = \xi + \frac{\pi}{2} + \rho$. Substituting $\varphi_{\bar{g}}$ and $\varphi_{\bar{i}}$ in (11″), we obtain the points g' and i'. The points of intersection of the straight line $\eta = \xi + \frac{\pi}{2} + \rho$ with the characteristics $\eta = \text{const}$ passing through g' and i' will be denoted as m' and s'.

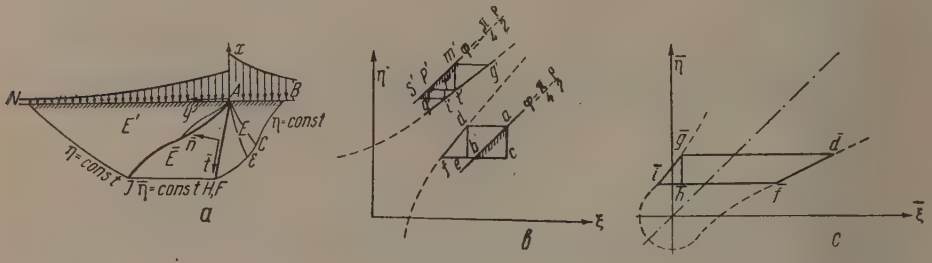

Fig. 1.

Then, performing the construction shown in Fig. 1, *b*, we obtain the points t', p', q', r'.

In the region $\bar{d}\,\bar{g}\,\bar{i}\,\bar{f}$ on the plane $(\bar{\xi}, \bar{\eta})$ we use the solutions (24)

$$y + x \operatorname{tg} \bar{\rho} = \Phi(\bar{\xi}), \quad x = \Psi(\bar{\eta}). \tag{a}$$

To the portion of the characteristic $\overline{dg}$ corresponds the point A on the plane (x, y) with the co-ordinates $(0, 0)$, therefore along $\bar{d}\bar{g}$

$$x = 0, \quad y = 0.$$

Hence, according to formulae (a), we see that

$$\Phi(\bar{\xi}) = 0 \quad \text{and} \quad y + x \operatorname{tg} \bar{\rho} = 0$$

in the trapezium $\bar{d}\bar{g}\bar{h}\bar{f}$. Thus, the trapezium $\bar{d}\bar{g}\bar{h}\bar{f}$ corresponds to the straight line $y + x \operatorname{tg} \bar{\rho} = 0$ on the plane (x, y) separating the region where hold the conditions (3) from the region where are satisfied the conditions (4).

The triangle $\bar{g}\bar{h}\bar{i}$ corresponds to the region $\bar{E}$ on the plane (x, y). Let us see how the stresses change after crossing this line denoted as AF in Fig. 1, *a*. For that purpose determine the stresses σ_n, σ_t, τ_{nt} along this line*.

In the formulae for stress component transformation which serve to pass to another system of co-ordinates:

$$\sigma_n = \sigma_x \cos^2\theta + \sigma_y \sin^2\theta + \tau_{xy} \sin 2\theta$$
$$\sigma_t = \sigma_x \sin^2\theta + \sigma_y \cos^2\theta - \tau_{xy} \sin 2\theta$$
$$\tau_{nt} = \frac{\sigma_y - \sigma_x}{2} \sin 2\theta + \tau_{xy} \cos 2\theta$$

* n and t respectively denote the normal and tangent to the line AF (Fig. 1, *a*).

let us substitute the formulae (20) and $\theta = \frac{\pi}{2} - \bar{\rho}$ to obtain

$$\sigma_n = -\sin\rho \operatorname{ctg}\bar{\rho}\,\bar{\eta} - \frac{\bar{K}}{\sin\bar{\rho}}$$

$$\sigma_t = \frac{2\sin\rho}{\sin 2\bar{\rho}}\,\bar{\xi} + \sin\rho \operatorname{tg}\bar{\rho}\,\bar{\eta} - \frac{\bar{K}}{\sin\bar{\rho}}$$

$$\tau_{nt} = \sin\rho\,\bar{\eta}.$$

From these formulae it may be seen that σ_n and τ_{nt} do not depend on $\bar{\xi}$ and, consequently, are constant along the characteristic $\bar{\eta} = \text{const}$ within the trapezium $\bar{d}\bar{g}\bar{i}\bar{f}$. Therefore σ_n and τ_{nt} have the same values at the points of the sections $\bar{d}\bar{f}$ and $\bar{g}\bar{h}$ lying on the same characteristic $\bar{\eta} = \text{const}$.

Hence it follows that σ_n and τ_{nt} are continuous at the boundary AF in the plane (x, y). The stress σ_t undergoes a jump at this crossing.

In the triangle def on the plane (ξ, η) we know the values of x, y along de, while the relation $y + x\operatorname{tg}\rho = 0$ holds along df. Solving the mixed problem, we obtain

$$x = x(\xi, \eta), \quad y = y(\xi, \eta) \tag{b}$$

in the triangle dfe.

Taking the functions (b) along df, $x[\xi_{II}(\varphi), \eta_{II}(\varphi)]$, and substituting $\varphi = \bar{\varphi}^*_{II}(\bar{\eta})$, we obtain

$$x\{\xi_{II}[\bar{\varphi}^*_{II}(\bar{\eta})], \quad \eta_{II}[\bar{\varphi}^*_{II}(\bar{\eta})]\} = x^*(\bar{\eta})$$

along $\bar{d}\bar{f}$ on the plane $(\bar{\xi}, \bar{\eta})$.

From the equality

$$\Psi(\bar{\eta}) = x^*(\bar{\eta})$$

we find Ψ in the trapezium $\bar{d}\bar{g}\bar{i}\bar{f}$. Thus

$$x = x^*(\bar{\eta}) \tag{c}$$

in the trapezium $\bar{d}\bar{g}\bar{i}\bar{f}$ and, consequently, along $\bar{g}\bar{i}$.

Taking the function (c) along $\bar{g}\bar{i}$, $x^*[\bar{\eta}_{III}(\varphi)]$, and substituting $\varphi = \varphi^*_{III}(\eta)$, we obtain

$$x = x^*\{\bar{\eta}_{III}[\varphi^*_{III}(\eta)]\}$$

along $g'i'$ in the plane (ξ, η). Along the portion of the characteristic $g'm'$

$$x = 0, \quad y = 0.$$

Solving in succession for the equations (5) of [1] the mixed problems in the triangles $g'm't'$, $m't'p'$, $t'r'i'$, the Goursat problem in the rectangles $r'p'q'i'$ and the mixed problem in the triangle $p's'q'$, we obtain

$$x = x(\xi, \eta), \quad y = y(\xi, \eta) \tag{d}$$

in the parallelogram $g'm's'i'$ in the plane (ξ, η).

Taking the function (d) along $g'i'$

$$x[\xi_{III}(\varphi), \eta_{III}(\varphi)], \quad y[\xi_{III}(\varphi), \eta_{III}(\varphi)]$$

and substituting $\varphi = \bar{\varphi}_{III}(\bar{\xi})$, we obtain

$$x\{\xi_{III}[\bar{\varphi}_{III}(\bar{\xi})], \eta_{III}[\bar{\varphi}_{III}(\bar{\xi})]\} = x_*(\bar{\xi}), \qquad y\{\xi_{III}[\bar{\varphi}_{III}(\bar{\xi})], \eta_{III}[\bar{\varphi}_{III}(\bar{\xi})]\} = y_*(\bar{\xi})$$

along $\bar{g}\bar{i}$ on the plane $(\bar{\xi}, \bar{\eta})$.

From the equality

$$y_*(\bar{\xi}) + x_*(\bar{\xi}) \operatorname{tg}\rho = \Phi(\bar{\xi})$$

we find Φ within the triangle $\bar{g}\bar{i}\bar{h}$. Thus, we obtain on the plane $(\xi, \bar{\eta})$

$$x = x^*(\bar{\eta})$$

$$y = y(\bar{\xi}, \bar{\eta}) = \begin{cases} y_*(\bar{\xi}) + [x_*(\bar{\xi}) - x^*(\bar{\eta})] \operatorname{tg}\bar{\rho} & \text{in the triangle } \bar{g}\bar{i}\bar{h} \\ -x^*(\bar{\eta}) \operatorname{tg}\bar{\rho} & \text{in the trapezium } \bar{d}\bar{g}\bar{h}\bar{f}. \end{cases}$$

Inverting the functions (d), we obtain

$$\xi = \xi(x, y), \quad \eta = \eta(x, y) \tag{e}$$

in the region E'. Along $m's'$, $\eta = \xi + \frac{\pi}{2} + \rho$, hence, we shall obtain

$$\sigma^*(y) = e^{\operatorname{tg}\rho\left(2\eta - \frac{\pi}{2} + \rho\right)}$$

along $m's'$, where $\eta = \eta(0, y)$ is taken from the formulae (e).

Consequently, according to formulae (13″) we find

$$\sigma_x(y) = \sigma^*(y)(1 - \sin\rho) - \frac{K}{\sin\rho}.$$

Exactly in the same way we solve the problem for the cases $\sigma_x'(y) < 0$ and $\sigma_x = \text{const}$ along AB. If the load along AB consists of several sections, within each of which it changes monotonously, the plane (ξ, η) will be many-sheeted and the reasoning advanced above will hold for this case.

The solution of the problem considered may be easily extended to the case when mass forces are present. In this case we introduce into the analysis the planes (α, β) and $(\bar{\alpha}, \bar{\beta})$, it being known that the plane (α, β) is two-sheeted.

In the region $\bar{E}$ (Fig. 1, *a*) we use the solutions (23). In the regions E and E' the extension of the problem considered above to the case of presence of mass forces is performed in the same way as in [1].

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CHEMISTRY

CALCULATION OF THE INTERMEDIATE EQUILIBRIA IN CATALYTIC KINETICS AND THE GEOMETRY SITUS

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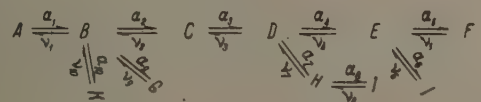
1. Introduction. Every one dealing with the kinetics of catalysis, particularly of a homogeneous catalysis, is in need of such methods, by whose mean the solution of the equations obtained could be brought about in a rapid and representative manner. In the majority of cases more or less complicated equilibria precede the irreversible slow stage which determines the velocity of the reaction. For the catalyst in these equilibria there is given only its summary concentration s in the case of homogeneous catalysis, or else its total active surface, which is a quite analogous value for the case of heterogeneous catalysis. In the kinetics it is necessary to express the concentration of the reaction-active form as the function s of the general concentrations and of the equilibrium constants so as to substitute the concentration of the reaction-active form thus obtained into the differential equation of the velocity of the irreversible stage. This calculation of intermediate equilibria, usually very tedious and not leading to lucid results, can be carried out so simply that it is sufficient to write down the reaction scheme in order to have already the solution. This method is quite general, it can be applied to all monomolecular and to certain cases of bimolecular reactions, successive as well as simultaneous ones, with all kinds of ramifications of the reaction scheme. It can be extended as well over other cases where equilibrium states are involved, for instance over adsorption.

2. Monomolecular Reactions. Let us consider, for instance, the following reaction scheme:



(2.1)

where Latin letters express the state, and Greek ones — the constants of the transition velocities. Suppose it is required to find the equilibrium concentration $[E]$ of a state E selected arbitrarily. The solution is

$$[E] = s\frac{Z}{N} \tag{2.2}$$

where

$$Z = \frac{\alpha_1\alpha_2\alpha_3\alpha_4}{\nu_1\nu_2\nu_3\nu_4} \tag{2.3}$$

and the denominator N equals the expression*:

$$1 + \frac{\alpha_1}{\nu_1}\left[_4\, 1 + \frac{\alpha_2}{\nu_2}\left[_3\, 1 + \frac{\alpha_3}{\nu_3}\left[_2\, 1 + \frac{\alpha_4}{\nu_4}\left[_1\, 1 + \frac{\alpha_5}{\nu_5}\right]_{(4)}\right.\right.\right. \tag{2.4}$$

$$\times \frac{\alpha_6}{\nu_6} \times \frac{\alpha_7}{\nu_7}\left[1 + \frac{\alpha_8}{\nu_8}\right]$$

$$\times \frac{\alpha_9}{\nu_9} \times \frac{\alpha_{10}}{\nu_{10}}$$

In scheme (2.1) and in expression (2.4) there exists a one-to-one correspondence between elements, and both (2.1) and (2.4) from the point of view of geometry situs are isomorphous with the tree (Fig. 1).

Fig. 1.

Fig. 2.

To the links of the tree in Fig. 1 there correspond the signs of equilibrium in the scheme (2.1) and the algebraic plus signs in the formula (2.4). To the vertices of the tree in Fig. 1 there correspond the chemical states $A, B, ..$ in the scheme (2.1), while in the formula (2.4) the corresponding elements are: a unity for the left vertex (the beginning or root of the tree). $\frac{\alpha_t}{\nu_t}\Big]_{(n)}$ and $\frac{\alpha_t}{\nu_t}\Big[_n\, 1$ for the right and the middle vertices, respectively. In some obvious cases the brackets can be omitted.

When writing scheme (2.1) all the branches should be turned to the right; this is required by the absence of the commutative law for the sign + and the bracket element $\frac{\alpha_t}{\nu_t}\Big[_n\, 1$ in the expression (2.1). If, besides, it is agreed to direct all the upper arrows in the signs of equilibrium to the right, then into the numerator of the element $\frac{\alpha_t}{\nu_t}\Big[_n\, 1$ and resp. $\frac{\alpha_t}{\nu_t}\Big]_n$ it is necessary to substitute the kinetic coefficient (i. e. in the case of a monomoleculr reaction—the velocity constant) of the formation α_t just of the state T which corresponds to this element as a vertex of the tree.

The calculation of scheme (2.1) is therefore effected by substitution of its elements with all the corresponding algebraic elements; the denominator of the solution is thus obtained. To present the results in the usual form it

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* In the expression (2.4) the obvious symbol $[_n$ express the opening of brackets of the n-th order, for instance, $[_1$ in ordinary expressions is (. In the same way $[_2 = [$; $[_3 = \{$. The sign $]_n$ express the closing of brackets of the n-th order. For a k-fold bracket from the 1st to the k-th order we write in the index (k). Another perspicuous sign in (2.4) is $1^{\times a}_{\times b}$, which equals $1 + a + b$.

remains only to write down all the members in one line, changing the signs of the brackets. Thus, (2.4) is transformed into:

$$N=1+\frac{\alpha_1}{\nu_1}\left(1+\frac{\alpha_9}{\nu_9}+\frac{\alpha_{10}}{\nu_{10}}+\frac{\alpha_2}{\nu_2}\left\{1+\frac{\alpha_3}{\nu_3}\left[1+\frac{\alpha_7}{\nu_7}\left(1+\frac{\alpha_8}{\nu_8}\right)+\right.\right.\right.$$
$$\left.\left.\left.+\frac{\alpha_4}{\nu_4}\left(1+\frac{\alpha_5}{\nu_5}+\frac{\alpha_6}{\nu_6}\right)\right]\right\}\right). \qquad (2.5)$$

In order to obtain Z in the numerator of the solution, it will suffice to write down one after another all the quantities $\frac{\alpha_t}{\nu_t}$ (in the case of monomolecular reactions, the equilibrium constants) starting from the root of the tree up to the state of the reaction, in the present case E. Their product will be Z (2.3). Side equilibria do not enter into Z. The beginning of the numeration, i. e. the root of the tree, can be chosen arbitrarily, but it must be the same for N and Z. If the beginning of the numeration is changed, both N and Z change too, but so as to leave the final result unaltered. If the beginning of the numeration coincides with the state in consideration, then $Z=1$.

The methods examined in this section can be applied, for instance, to a case when a substance reacts in a definite adsorption state, the surface of the catalyst being completely covered.

3. Bimolecular Reactions. A bimolecular reaction $A+B=C$ will be designed as follows:

$$\left.\begin{matrix}A\\B\end{matrix}\right\}\underset{\nu}{\overset{\alpha}{\rightleftarrows}}C. \qquad (3.1)$$

The scheme of a complicated bimolecular reaction can be expressed graphically as well. Such a scheme is reduced to a tree of monomolecular reactions in cases when the concentration of one of the substances participating in the bimolecular reaction (3.1), say $[A]$, is known and the sum of the other concentrations is known as well, say $[B]+[C]=s$. It is just with such cases that one has to deal with in catalysis. This reduction can be carried out through the substitution of the kinetic coefficient $\beta=\alpha[A]$ for the velocity constant α. We shall understand under the kinetic coefficient in the case of monomolecular reactions—the velocity constant of reactions, and in the case of bimolecular reactions—the product of the velocity constant by the known concentration of the other substance. Then (3.1) will be equivalent to the monomolecular scheme

$$B\underset{\nu}{\overset{\beta}{\rightleftarrows}}C \qquad (3.2)$$

and the calculation of this scheme can be carried out according to the rules given above for monomolecular reactions. Thus, from (3.2) which is isomorphous with the simplest tree or with a 1-dimensional simplex (Fig. 2) we find through substitution that

$$N=1+\beta/\nu=1+\alpha[A]/\nu;\ Z=\beta/\nu=\alpha[A]/\nu \qquad (3.3)$$

$$[C]=s\frac{\alpha[A]/\nu}{1+\alpha[A]/\nu} \qquad (3.4)$$

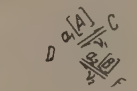
This is nothing else but the adsorption isotherm of Langmuir for a heterogeneous system, and this equation, as follows from the deduction, does not differ from the equation which one often encounters in homogeneous catalysis involving an intermediate equilibrium.

When two gases A and B are being adsorbed, then

$$\left.\begin{matrix} A \\ D \end{matrix}\right\} \underset{\nu_1}{\overset{\alpha_1}{\rightleftarrows}} C, \qquad \left.\begin{matrix} B \end{matrix}\right\} \underset{\nu_2}{\overset{\alpha_2}{\rightleftarrows}} F \tag{3.5}$$

where $[D]+[C]+[F]=s$ (s being the total area of the solid, $[A]$—the pressure of one gas and $[B]$—that of the other one). Let $[C]$ be the unknown.

According to the above, this bimolecular scheme is equivalent to a monomolecular one



$$\text{wherefrom} \qquad N=1+\frac{\frac{\alpha_1}{\nu_1}[A]}{\frac{\alpha_2}{\nu_2}[B]}, \quad Z=\frac{\alpha_1}{\nu_1}[A] \tag{3.6}$$

and

$$[C]=s\frac{\frac{\alpha_1}{\nu_1}[A]}{1+\frac{\alpha_1}{\nu_1}[A]+\frac{\alpha_2}{\nu_2}[B]}. \tag{3.7}$$

Then passing over to the scheme

$$\left.\begin{matrix} A \\ B \end{matrix}\right\} \underset{\nu}{\overset{\alpha}{\rightleftarrows}} \left\{\begin{matrix} C \\ D \end{matrix}\right. \tag{3.8}$$

we see that under the condition that $[B]+[C]=s$, it is equivalent to

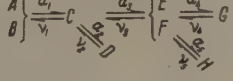
$$B \underset{\nu[D]}{\overset{\alpha[A]}{\rightleftarrows}} C, \tag{3.9}$$

wherefrom

$$[C]=s\frac{\frac{\alpha}{\nu}[A]}{1+\frac{\alpha}{\nu}[A]}. \tag{3.10}$$

In the vertices of the monomolecular scheme which is obtained from the bimolecular one, are placed just those states whose concentrations' sum equals s.

4. Mixed Schemes. Under mixed schemes, which are met with most often, we shall understand schemes of simultaneous-successive equilibrium reactions, consisting both of mono- and bimolecular stages. The method for their calculation is clear from what has been said above. We give here only one example. Let $[F]$ be the unknown in a mixed scheme

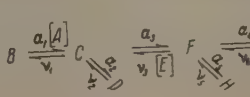


(4.1)

whereby

$$[B]+[C]+[D]+[F]+[G]+[H]=s. \tag{4.2}$$

Scheme (4.1) is equivalent to the monemolecular one



(4.3)

On the base of isomorphism

$$N = 1 + \frac{\alpha_1 [A]}{\nu_1} \left[1 + \frac{\alpha_2}{\nu_2 [E]} \left(1 + \frac{\alpha_4}{\nu_4} \right) \right] \tag{4.4}$$

$$Z = \frac{\alpha_1 [A]}{\nu_1} \cdot \frac{\alpha_3}{\nu_3 [E]} \tag{4.5}$$

wherefrom

$$[F] = s \frac{Z}{N} = s \frac{\frac{\alpha_1}{\nu_1} \frac{\alpha_3}{\nu_3} \frac{[A]}{[E]}}{1 + \left(\frac{\alpha_1}{\nu_1} + \frac{\alpha_1 \alpha_2}{\nu_1 \nu_2} \right) [A] + \left(\frac{\alpha_1 \alpha_3}{\nu_1 \nu_3} + \frac{\alpha_1 \alpha_3 \alpha_4}{\nu_1 \nu_3 \nu_4} + \frac{\alpha_1 \alpha_3 \alpha_5}{\nu_1 \nu_3 \nu_5} \right) \frac{[A]}{[E]}}. \tag{4.6}$$

In order to characterize the simplicity of this method we may point out that all the calculations of such a complex case are given at full length, without omitting any supplementary calculations.

5. Proof of the General Case. The elementary proof of the method examined above is based upon the study of the course of the solution of equations formed on the base of the reaction scheme of equilibria taken as a general case.

Suppose that for any number of states we have a reaction scheme, for the present with one branch only:

$$\begin{gathered} X_1 \overset{a_1}{\rightleftharpoons} X_2 \overset{a_2}{\rightleftharpoons} X_3 \overset{a_3}{\rightleftharpoons} \ldots \\ \ldots \overset{a_{r-2}}{\rightleftharpoons} X_{r-1} \overset{a_{r-1}}{\rightleftharpoons} X_r \overset{a_r}{\rightleftharpoons} X_{r+1} \overset{a_{r+1}}{\rightleftharpoons} \ldots \overset{a_{n-1}}{\rightleftharpoons} X_n \\ \overset{b_1}{\rightleftharpoons} Y_1 \overset{b_2}{\rightleftharpoons} Y_2 \overset{b_3}{\rightleftharpoons} \ldots \overset{b_m}{\rightleftharpoons} Y_m \end{gathered} \tag{5.1}$$

To each equilibrium state X_i and Y_i there corresponds a concentration x_i and y_i, the total sum of which is s; a_i are ratios of kinetic coefficients. Let x_r—the concentration of the state X_r which for generality sake is selected beyond the ramification—be the unknown. For the $n + m$ unknowns we have a system of $n + m$ equations (5.2).

$$\left.\begin{array}{lll} (1) & s = x_1 + x_2 + x_3 + \ldots & \\ & \quad \ldots + x_{r-1} + x_r + x_{r+1} + \ldots + x_n & \\ & \quad \times y_1 + y_2 + \ldots + y_m & \\ (2) & a_1 x_1 = x_2 & x_1 = x_2/a_1 = x_r/(a_1 \ldots a_{r-1}) \\ (3) & a_2 x_2 = x_3 & x_2 = x_3/a_3 = x_r/(a_2 \ldots a_{r-1}) \\ \ldots & \ldots & \ldots \\ (r-1) & a_{r-2} x_{r-2} = x_{r-1} & x_{r-2} = x_{r-1}/a_{r-2} = x_r/(a_{r-2} a_{r-1}) \\ (r) & a_{r-1} x_{r-1} = x_r & x_{r-1} = x_r/a_{r-1} \\ (r+1) & a_r x_r = x_{r+1} & x_{r+1} = a_r x_r \\ (r+2) & a_{r+1} x_{r+1} = x_{r+2} & x_{r+2} = a_{r+1} a_r x_r \\ \ldots & \ldots & \ldots \\ (n) & a_{n-1} x_{n-1} = x_n & x_n = a_{n-1} \ldots a_r x_r \\ \hline (n+1) & b_1 x_{r-1} = y_1 & y_1 = b_1 x_{r-1} = b_1 x_r/a_{r-1} \\ (n+2) & b_2 y_1 = y_2 & y_2 = b_2 y_1 = b_1 b_2 x_r/a_{r-1} \\ \ldots & \ldots & \ldots \\ (n+m) & b_m y_{m-1} = y_m & y_m = b_m y_{m-1} = b_1 \ldots b_m x_r/a_{r-1} \end{array}\right\} \tag{5.2}$$

The commutative law for the sum gives the possibility to dispose the members in equation (1) of the system (5.2), the number of which equals the number of states, in whichever order one likes, and particularly in the form of the reaction tree of scheme

(5.1). Until now this order is arbitrary. The remaining $n+m-1$ equations connect into pairs every two adjoining unknowns. The course of the solution consists in expressing each one of them through the unknown x_r. This is accomplished in the next (right) column. Then these values are substituted for into equation (r) of the system (5.2) and x_{r-1} is expressed through x_r. The coefficient a_{r-1} appears in the denominator. We remark that while coming gradually up, the foregoing coefficient is every time introduced additionally into the denominator until we reach $x_1=x_r/(a_1 \ldots a_{r-1})$. And vice versa, when coming down, the next coefficient is introduced every time as a factor. All the x and y are positive and consist of one member. Therefore when their meaning is substituted for into equation (r) of the system (5.2), its form as a tree does not change and all the signs are positive:

$$s = x_r\left(\frac{1}{a_1 \ldots a_{r-1}} + \frac{1}{a_2 \ldots a_{r-1}} + \ldots + \frac{1}{a_{r-2}a_{r-1}} + \frac{1}{a_{r-1}} + \right.$$
$$+ 1 + a_r + a_r a_{r+1} + \ldots + a_r \ldots a_n$$
$$\times$$
$$\left.\frac{b_1}{a_{r-1}} + \frac{b_1 b_2}{a_{r-1}} + \ldots + \frac{b_1 \ldots b_m}{a_{r-1}}\right) \qquad (5.3)$$

In order to clear of fractions we multiply both parts of the equation by the denominator of the first member:

$$a_1 \ldots a_{r-1} s = x_r (1 + a_1 + a_1 a_2 + \ldots +$$
$$+ a_1 \ldots a_{r-2} + a_1 \ldots a_{r-1} + a_1 \ldots a_r + a_1 \ldots a_{r+1} + \ldots + a_1 \ldots a_n) \qquad (5.4)$$
$$\times$$
$$a_1 \ldots a_{r-2} b_1 + a_1 \ldots a_{r-2} b_1 b_2 + \ldots + a_1 \ldots a_{r-2} b_1 \ldots b_m.)$$

The member may still be commuted, but in that case their natural order would be broken. When moving from left to right in the right part of the equation (5.4), in every member there appears a new coefficient a as a factor, so that in every member the subscripts form a natural series of number s. This proceeds up to the member $a_1 \ldots a_{r-2}$, and then a ramification takes place. Moving along one branch, we continue to accumulate one after another the coefficients a, and moving along the other branch we accumulate already the coefficients of this branch, b. This takes place because the system of the equations from (r) to (n)-th in (5.2), on one hand, and from $(n+2)$ to (m)-th in (5.2). on the other hand, are separate systems of equations connected with the former system from (2) to $(r-2)$-th equation only by means of the connecting equations $(r-1)$ and $(n+1)$-th .This is the cause of the isomorphism existing between the reaction tree and the tree N.

Solving (5.4) relatively to x_r and introducing an abbreviated bracket sign from Section 2, we obtain finally:

$$x_r = s\,\frac{a_1 \ldots a_{r-1}}{1+a_1[1+a_2[1+\ldots+a_{r-3}[1+a_{r-2}[1+a_{r-1}[1+a_r[1+a_{r+1}[1+\ldots+a_{n-1}]}} \qquad (5.5)$$
$$\times$$
$$b_1[1+b_2[1+\ldots+b_m]$$

(the subscripts of the brackets, as being obvious by themselves, are omitted here). The numerator is a product of all the a one after the other from the first one to the reaction state X_r [see scheme (5.1)] and in the denominator we have a tree isomorphous with the tree of scheme (5.1), the elements of which coincide with those considered in Section 2. Here the isomorphism is already fixed; the elements cannot be commuted.

In the proof no restrictions are imposed upon the choice of the place of the ramification. Therefore an analogous result will be general for any place of the ramification. If there are several ramifications, then, besides the equations $(n+1) \ldots (n+m)$ in (5.2), there will appear quite analogous equations for the new branches, and on similar reasoning we shall come to a quite analogous expression for x_r, but with new ramifications. Les us note here that no restrictions have been placed upon the start of numeration. Therefore the choice of the latter is arbitrary; every time there will be identical expressions, but under different forms.

Thus, we have obtained the rules given in Section 2 and in the following ones, and that is what we had to prove.

For an u n r a m i f i e d tree of equilibria, as it follows from the above, the concentration g_k of a definite state can be expressed as

$$g_k = \frac{\prod_0^k a_j}{\sum_0^n \prod_0^j a_j} \qquad (5.6)$$

if we take that $a_0=1$. In this case n is the number of all the states (not counting the zero one), j—the current number of the state, k—the number of the state that interests us. We have a particular case when all the a_j are i d e n t i c a l: $a_j=a$. Then (5.6) is transformed into

$$g_k = \frac{a^k}{\sum_0^n a_j^j} = \frac{a^k}{1+a+a^2+\ldots+a^n} = \frac{a^k(1-a)}{1-a^{n+1}} . \qquad (5.7)$$

It is essential that the scheme (5.1) should be actually a tree, and not a net, i. e. there must be no closed (cyclic) ways. In a contrary case these connecting links give additional equations in (5.2) compared with the number of unknowns, i. e. they introduce only certain additional relations between the constants. This agrees completely with chemical facts, because between two states it is quite sufficient to have one communication, even if the latter is distant, consisting only of equilibria, so as to establish an equilibrium between these states as well.

The principle of isomorphous substitution applied in the present paper has already been used by the first founders of scientific chemistry, though no one appears to have noticed this. We have in mind the substitution of chemical s y m b o l s of atoms and elements in a stoicheiometric equation with the q u a n t i t i e s of the atomic weights (at that time—of combining weights) in solving the problems concerning weight relations. In modern times the law of mass conservation has undergone changes which have to be taken into consideration, particularly in the case of the reactions of atomic nuclei. But, on the other hand, in this latter case that principle has been applied to the charges of atomic nuclei.

C o n c l u s i o n

A method has been devised, very simple and clear in its application, for the calculation of simultaneous-successive intermediate equilibria in homogeneous and heterogeneous catalysis, based on the topological conception of the isomorphism existing between the reaction tree and the tree of the solution.

Examples of its practical application will be given in another paper.

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CHEMISTRY

NITROSYL COMPOUNDS OF PLATINUM

By A. GELMAN and Z. P. MAXIMOVA

(Communicated by N. S. Kurnakov, Member of the Academy, 29. VI. 1939)

The assumption expressed by one of us (1) about the high transactiveness of nitric oxide (NO) in the inner sphere of the complex needed experimental confirmation. In this article we made it our aim to produce and study those complex compounds of platinum and NO which are analogous to Zeise's compounds(2). Although we did not find any indications in literature as to the existence of such compounds, it might have been expected that nitric oxide being a unsaturated molecule should behave in co-ordinational addition like carbon monoxide or the ethylene hydrocarbons.

The method of production of platinum nitrosyl compounds is as follows: a saturated solution of potassium or ammonium chlorplatinite was put into an Erlenmeyer flask; after displacing the air out with a current of carbon dioxide the flask was joined to a gasometer with NO which in its turn displaced CO_2. After this the flask was stoppered tightly and the chlorplatinite solution was under a slight pressure of nitric oxide. The reaction was performed at room temperature. In 10—12 hours the chlorplatinite solution began to turn brown and upon further standing became green-tinged. On the surface of the solution and at the bottom of the flask there appeared a brownish-red crystalline precipitate.

On the basis of a number of experiments it can be stated that the reaction of instillation of NO in chlorplatinite is completed in about 3—4 days. The course of the reaction is assumed to be as follows:

$$Me_2[PtCl_4] + NO \rightarrow Me\,[PtNOCl_3] + MeCl.$$

After three—four days the NO was no longer admitted into the flask and the latter was again filled with carbon dioxide. The brownish-red precipitate mentioned above was filtered, washed, dried and analyzed. We found that it was a mixture of chlorplatinite and some substance of indefinite composition.

The filtrate which, according to our assumption, contains a solution of $Me\,[PtNOCl_3]$ was divided into two parts. When the aqueous solution of the chloride of Reise's first base had been added to one of them, there immediately appeared a small-grained precipitate of reddish-grey colour. The reaction expected is:

$$2Me\,[PtNOCl_3] + [Pt4NH_3]\,Cl_2 \rightarrow [Pt4NH_3]\,[PtNOCl_3]_2 + 2MeCl;$$

After being washed many times with water and alcohol the precipitate was dried in the exsiccator and analyzed. The platinum content in this substance fluctuated in various tests (8 tests in all) from 63.67 to 64.4%.

Calculated Pt=63.2%. Cl found 23.2%, 23.37%, Cl calculated 23.72%. N found 9.4%, N calculated 9.06%.

The analysis data confirm the fact that we obtained $[Pt4NH_3]\,[PtNOCl_3]_2$, a substance analogous to that produced by Jörgensen with Zeise's salt ([3]), and so does the interchange reaction with potassium chlorplatinite:

$$[Pt4NH_3]\,[PtNOCl_3] + K_2PtCl_4 \rightarrow [Pt4NH_3]\,[PtCl_4] + 2K\,[PtNOCl_3].$$

Pyridine was carefully added to the other part of the Me $[PtNOCl_3)$ solution, and each drop immediately caused the appearance of a light-green precipitate. In analogy to ethylene and carbonyl compounds the following reaction was expected:

$$Me\,[PtNOCl_3] + Py \rightarrow [PtNOPyCl_2] + MeCl$$

which was confirmed by analysis. The light-green coloured precipitate was filtered, washed with water, dried over $CaCl_2$ and analyzed. The non-recrystallized substance contained from 50 to 51% Pt. Recrystallized from hot alcohol—from 51.5 to 51.62%. Calculated for $[PtNOPyCl_2]$, Pt=52.03%. Found N=7.04%, calculated N=7.4%. It is curious to note that in determining chlorine in this compound we observed the same picture as in the case of $[PtCOPyCl_2]$, i. e., after the complex had been decomposed $AgNO_3$ precipitated only $^2/_3$ of the chlorine contained in the substance being analyzed according to calculation. Reducing with zinc in H_2SO_2 we obtained Cl=12.26 and 12.6%; baking with soda, 13.59%; the per cent of chlorine rose to 15.36 when the substance under analysis was oxidized with hydrogen peroxide before reducing with zinc, and to 15.11 when oxidized with H_2O_2 before baking with soda. For $[PtNOPyCl_2]$ we calculated Cl=18.91%. One third of the chlorine evidently goes to form some volatile compound.

In trying to obtain more accurate figures in analyzing this substance, we synthesized it more than ten times. However, in spite of the fact that precipitation with pyridine goes on very smoothly, the substance almost always becomes impure with something (possibly $PtPy_2Cl_2$) and recrystallization is necessary.

P r o p e r t i e s o f $[PtNOPyCl_2]$. In external appearance this is a small-grained substance of light-green colour. It reacts weakly with dilute hydrochloric acid in the cold, but upon being heated dissolves in a few minutes:

$$[PtNOPyCl_2] + HCl \rightarrow PyH\,[PtNOCl_3].$$

From the cooled solution pyridine again precipitates the initial dichloride. Consequently, just as in the case of ethylene and carbonyl compounds we have to do with the equilibrium

$$[PtNOPyCl_2] \underset{Py}{\overset{HCl}{\rightleftarrows}} PyH\,[PtNOCl_3]$$

which in this case is due to the high transactiveness of the NO molecule. The existence of this equilibrium already makes us assume that $[PtNOPyCl_2]$ has a transconfiguration. However, this can be proved in another way as well.

N. S. Kurnakov's reaction for the immediate determination of the configuration of nitrosyl pyridine platinum dichloride cannot be applied in this case, since thiourea immediately displaces NO (just as ethylene and CO) and forms a characteristic precipitate of $Pt4ThCl_2$ yellow in colour. When $[PtNOPyCl_2]$ is dissolved in pyridine, gas bubbles are generated and a small pale-yellow precipitate appears. Adding distilled water promotes the

formation of the precipitate. The pale-yellow precipitate turned out to be $(PtPy_2Cl_2]$, consequently, the reaction took place according to the equation:

$$[PtNOPyCl_2] + Py \rightarrow [PtPy_2Cl_2] + NO\uparrow$$

Platinum dipyridine dichloride reacts with thiourea according to the equation:

$$[PtPy_2Cl_2] + 4Th \rightarrow \left[\begin{matrix} Py & & Th \\ & Pt & \\ Th & & Py \end{matrix}\right] + 2Th$$

precipitating a snow-white crystalline substance. This means that it had a transconfiguration which it could have obtained only by way of inheritance from $[PtNOPyCl_2]$. The transform of the $[PtNOPyCl_2]$ is borne out by the electroconducting of this compound which turned out to be a non-electrolyte.

$$\mu_{60'}^{10000} = 27.9; \quad \mu_{21\ hrs}^{10000} = 87.3$$

The solution of this substance is connected with the hydratation process. $[PtNOPyCl_2]$ dissolves well in hot alcohol which particular can be turned to amount in recrystallization; it is insoluble in water and does not decompose even when boiled.

Attempts to produce [PtNOClPyCl] (cis) were unsuccessful. When an aqueous solution of Kossa's pyridine salt $Me[PtPyCl_3]$ was treated with nitric oxide, a little small-grained pale green precipitate appeared at the bottom of the flask in 2—3 hours. When NO was displaced with carbon dioxide, the precipitate turned green sharply as a result of the change in the composition of the substance. The synthesis was repeated three times with the same result.

In analyzing various tests we found Pt=49.64, 51.97 and 53.41%; Cl=16. 74% and N=6.09%.

When Kossa's ammonia salt $Me[PtNH_3Cl_3]$ was treated under the same conditions with nitric oxide, violet crystals began to appear in abundant quantity after about 3—5 hours. The experiment was repeated twice. Washed and dried to constant weight, the violet substance contained:

	Pt, %	Cl, %	N, %
In the first test	68.4	17.59	8.07
In the second test	68.7	17.98	7.85

Although the analysis results of two separately synthesized tests coincide, all the same we do not take the liberty to give this substance any definite formula. Attention should be paid to the fact that when $Me(PtNOCl_3)$ is treated with ammonia, a dark violet precipitate also appears, but it is an insignificant one. A preliminary analysis of this substance showed that it contains 66% platinum. A more elaborate study of the violet substances is planned to be made in the near future.

The production of platinum nitrosyl compounds is connected with great difficulties, in spite of the fact that they are more stable in comparison to the ethylene and carbonyl compounds. The trouble is that they often contain some kind of admixtures which cannot be separated. Great precautions have to be taken in analyzing nitrosyl complexes, decomposing them first of all with ammonia or oxidizing them with hydrogen peroxide. These difficulties in working with nitrosyl compounds are, probably, connected with the electronic structures of nitric oxide, which has an uneven number of electrons on the outer orbit.

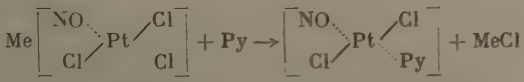
However, in spite of all, the platinum nitrosyl compounds produced by us, $Me[PtNOCl_3]$ and $[PtNOPyCl_2]$, in all their behaviour resemble the correspon-

ding ethylene and carbonyl molecules. Nitrous oxide N_2O does not react with the chlorplatinite, although the latter was kept under N_2O about 2 weeks. Apparently, N_2O is really an isoster of CO_2 in its electronic configuration and like the latter is not inclined to co-ordinational addition.

Conclusions

1. Nitrosyl platinum compounds of the type of Zeise's salts: $[Pt4NH_3][PtNOCl_3]_2$ and $[PtNOPyCl_2]$ have been produced.

2. The transconfiguration of $[PtNOPyCl_2]$ obtained according to the equation:



has been determined.

3. A high transactiveness of NO in the inner sphere has been established.

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CHEMISTRY

ANALYSIS OF MIXTURES CONTAINING PRIMARY POTASSIUM AND PRIMARY AMMONIUM PHOSPHATE

By D. I. KUZNETZOV and A. A. KOZHUKHOVSKY

(Communicated by N. S. Kurnakov, Member of the Academy, 29. VI. 1939)

In studying the solubility and the vapour tension in the system KH_2PO_4—$NH_4H_2PO_4$—H_2O one has to do with the quantitative determination of potassium, ammonium and phosphoric acid.

The salts used in this work were chemically pure for analysis. They were recrystallized threefold and dried at 100°. Primary ammonium phosphate had to be dried at 100° because it was necessary to attain a stoicheiometric composition, and if it were dried at ordinary temperature, it would not be freed of admixtures of the secondary phosphate. Drying primary potassium phosphate at 100° drove off all the hygroscopic water.

Experiment showed that if 10 cm^3 of a solution containing from 0.1 to 0.3 g and even more KH_2PO_4 or $NH_4H_2PO_4$ is evaporated, after 6 hours of drying at 100° we get a practically anhydrous salt corresponding to the stoicheiometric composition. If both salts are present in the solution, the sum of the salts can be determined in the same manner with accuracy greater than 0.1% of the value sought.

In this case ammonium was determined by driving off ammonia and then titrating. Determining potassium presents the greatest difficulties. The reason for this is the presence of PO'''_4 and $NH^{\cdot}$ ions in the solution. If potassium is determined in the form of $KClO_4$, most authors write that it is necessary first of all to remove ammonium.

In our experiments exaggerated values were invariably obtained when determining potassium as perchlorate in the presence of ammonium. We set ourselves the problem of finding a more convenient method of removing ammonium.

First of all we performed experiments on removing the ammonium immediately by heating. After heating for 24 hours at 250° the ammonium was not driven off. Of course, if calcined strongly at 600—800° ammonium is driven off; but then polymers of potassium metaphosphate are ormed. These compounds dissolve in water very slowly (in more than 24 hours); more quickly when boiled with HNO_3 or with HCl. If, however, the dry salt is heated in an evaporating dish over a Bunsen burner, ammonium is comparatively easy to drive off, but insignificant quantities of potassium metaphosphate polymers are nearly always formed. This last method may, apparently, give good results, if the conditions of the formation of insoluble metaphosphates are studied and optimal temperatures established for the removal of ammonium. It should be noted that potassium metaphosphate corrodes porcelaine and therefore platinum vessels should be used.

Then the following method was tried. $HClO_4$ was added to solutions of the phosphates and $KClO_4$ was removed as usual with an admixture of NH_4ClO_4.

The precipitate was filtered, calcined and then dissolved in water. The solution was evaporated dry and calcined; in calcining the salt often spurts, and besides there are light explosions and it is quite difficult to evade losses during them. After calcining KCl was produced and the per cent of K was calculated from it. This method does not give good results and is long and tedious, besides.

Ammonium is often removed by boiling with alkalis, e. g. with NaOH. Then potassium is determined in the form of the perchlorate. In checking this method we obtained good results, although it was necessary to evaporate carefully.

$HClO_4$ was added in excess, for if this is not done, $NaClO_4$ stays in the precipitate and cannot be washed out even after washing many times.

In view of the defects of these methods, another method was worked out, based upon the decomposition of ammonium salts with aqua regia. We were led to work out this method by the applied procedure of removing ammonium chloride by means of HNO_3[1].

The work of Vassiliev, Ravdin and Lukyanova [2] was devoted to the problem of the reaction between ammonium chloride and nitric acid. From this work it is evident that ammonium can be removed from NH_4Cl at 100° with nitric acid, with nitrogen coming off in the form of N_2 and NOCl. It was natural to assume that in the mixture: HNO_3, HCl and $NH_4H_2PO_4$, as a result of the presence of HNO_2 the ammonium salts would enter into reaction and free nitrogen would come off. Experiments showed that ammonium is completely removed from the ammonium phosphate. Potassium was determined in the following manner. Part of the solution, containing from 0.1 to 0.2 g potassium, was evaporated in a small Erlenmeyer flask (evaporating in a beaker is less convenient). Then, if the weighed portion of $NH_4H_2PO_4$ was not more than 0.1 g, 1—2 cm^3 aqua regia is added and the solution is heated gently at first and then evaporated dry. This procedure was repeated three times. The last time evaporation was discontinued after the odour of HCl and HNO_3 had disappeared. 2—3 cm^3 $HClO_4$ was added to the test and then 5—6 cm^3 H_2O. Water was added in such quantity that the $KClO_4$ precipitated upon adding $HClO_4$ should dissolve completely when heated. The solution was evaporated until heavy vapours of $HClO_4$ appeared, and then shaken while being cooled. When the solution had cooled down completely, 10 cm^3 of alcohol containing 0.2% $HClO_4$ were added. The precipitate was ground with a stirring rod, filtered through a glass filter with a porous bottom and dried for 15—20 min. at 130—150.

The results obtained were quite good. Their accuracy was the same as that attained in the usual method of determining potassium in the form of perchlorate.

The advantages of this method are that ammonium is removed by means of reagents which are the most accessible for the laboratory, and no new cation is introduced, as in the case of removing ammonia by means of NaOH.

P_2O_5 was determined not in the form of $Mg_2P_2O_7$ as usual, but immediately in the form of $MgNH_4PO_4.6H_2O$. This method has not yet found wide application, in spite of the fact that it is mentioned in literature. The results obtained by this method are no worse in accuracy than those obtained by determining P_2O_5 in the form of $Mg_2P_2O_7$.

The determination was made in the following manner. $MgNH_4PO_4.6H_2O$ was precipitated after Schmitz' method. The solution was left over night, since experience showed that not the hexahydrate, but a less hydrated salt

precipitates from the solution when hot. Then it was filtered through a glass filter with a porous bottom, washed three times with a 2 *n* solution of ammonia, three times with 96% alcohol and, finally, three times with ether. After standing in the air 10—15 min. the crucible was weighed.

In this procedure it is not necessary to apply the widespread method of burning the filter. The use of the latter considerably protracts the time necessary for the analysis.

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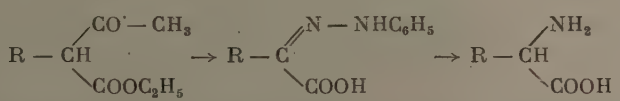
CHEMISTRY

SYNTHESIS OF α-AMINOACIDS BY MEANS OF ALKYLACETOACETIC ESTERS. I

By V. V. FEOFILAKTOV

(Communicated by N. D. Zelinsky, Member of the Academy, 25. VI. 1939)

In a previous paper(1) we have expressed the assumption that coupling the derivatives of α-acetobutyrolactone with diazocompounds, a procedure upon which the preparation of α-amino-γ-hydroxy-δ-chlorovaleric acid and from it of hydroxyproline is based, may be used as a general method for the preparation of α-aminoacids from alkylacetoacetic esters, according to the following scheme:



Only few indications, concerning the formation of phenylhydrazones of α-ketoacids starting from alkylacetoacetic esters are to be found in the literature.

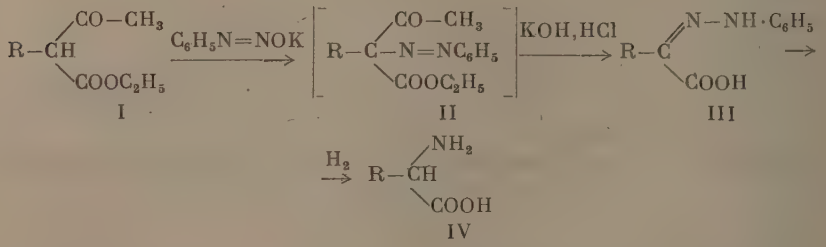
Thus, Japp and Klingemann(2), while studying the structure of the so-called «mixed azocompounds», acted with aqueous solution of diazonium chloride upon the alcohol solution of Na-derivatives of methylacetoacetic and ethylacetoacetic esters, and obtained phenylhydrazones of the pyruvic and the α-ketobutyric acid, respectively.

The same authors obtained α-phenylhydrazine-propionic acid by reducing the phenylhydrazone of pyruvic acid with a Na-amalgam and, in agreement with Fischer's indications(3), found small amounts of aniline to form here. When the same phenylhydrazone was being reduced more vigorously by means of a Na-amalgam, these authors stated that next to aniline small amounts of a hydrazone acid and of alanine were forming.

The observations of these authors were of a purely qualitative character, their aim being to investigate the nature of the coupling products of phenyldiazonium with alkylacetoacetic esters.

Our assumption concerning the possibility of using this process as a general method of the preparation of α-aminoacids by way of the phenylhydrazones of α-ketoacids has been supported by a successfull synthesis of the following α-aminoacids: alanine from methylacetoacetic ester; isoleucine and alloisoleucine from sec.-butylacetoacetic ester; leucine from isobutylacetoacetic ester; phenylalanine from benzylacetoacetic ester.

The coupling of alkylacetoacetic esters (I) with phenyldiazonium was carried out in an aqueous alkali solution in the cold during 4—6 hours; the coupling product—a reddish brown oil (having presumably structure II)—was extracted with ether and hydrolyzed directly with alcoholic-aqueous alkali. After the elimination of the alcohol and acidification the phenylhydrazone of the α-ketoacid (III) separated as a precipitate or brownish oil, that was quickly transformed into a mass of yellow crystals.



The reduction of the phenylhydrazone (III) was carried out in an alcohol solution with Zn-dust and an alcohol solution of hydrogen chloride in the cold (0°) during 6—8 hours. After the elimination of the alcohol and of the excess of hydrogen chloride through distillation under reduced pressure, the residue was treated in an aqueous solution at first with lead carbonate, then with silver carbonate, the filtrate was freed from silver by means of hydrogen sulphide and after evaporation the free α-aminoacid (IV) was obtained.

Isoleucine and Allo-isoleucine. The initial sec.-butylacetoacetic ester had the following properties: b. p. 105—106°/17 mm, 211—212°/752 mm; $n_D^{21.5}=1.4287$; $d_4^{21.5}=0.9599$; $MR=49.96$, calculated for the ketoform 50.04; for the enolic one 51.09 (without the exaltation). The coupling product with phenyldiazotate was hydrolyzed and acidified. There separated a reddish-brown precipitate which after crystallization from 80% acetic acid yielded a crystalline phenylhydrazone of methylethylpyruvic acid.

The yield was 63% of the theoretical amount. The melting point of the phenylhydrazone was 142—142.5°, which agrees with the m. p. mentioned in the literature(4). With concentrated sulphuric acid and potassium bichromate it gives a red-violet coloration. Nitrogen found 12.77 and 12.76%; calculated for $C_{12}H_{16}O_2N_2$—12. 73%.

Its reduction in an alcohol solution with zinc dust and HCl gave with a theoretical yield a mixture of isoleucine and allo-isoleucine, a colourless mass of crystals. Isoleucine was separated from allo-isoleucine through a repeated process of dissolving the mixture in water and precipitating the isoleucine with alcohol. Through the evaporation of the alcoholic-aqueous mother liquids allo-isoleucine was obtained. For further purification allo-isoleucine was crystallized from water in which it is more soluble than isoleucine.

Isoleucine: m. p. 286° (in a sealed tube), nitrogen found 10.68, 10.90%; calculated for $C_6H_{13}NO_2$—10.69%.

Allo-isoleucine: m. p. 275—6° (in a sealed tube), nitrogen found 10.70, 10.92%; calculated for $C_6H_{13}NO_2$—10.69%.

Leucine. The initial isobutylacetoacetic ester had the following properties: b. p. 94—95°/8 mm; $n_D^{18.5}=1.4288$; $d_4^{18.5}=0.9535$; $MR=50.31$; calculated for the ketoform 50.04; for the enolic one 51.09 (without the exaltation).

After the coupling with phenyldiazotate and the hydrolysis of the coupling product, the reaction mixture was acidified and the phenylhydrazone of isopropylpyruvic acid separated at once as a mass of yellow crystals. Yield—72.5% of the theoretical amount. With concentrated sulphuric acid and potassium bichromate these crystals give a violet coloration (Bülow reaction). They have no sharp melting point and begin to melt from 97° on. Plattner([5]), who has described this phenylhydrazone obtained from isovalerylformic acid, did not give its melting point.

Through crystallization from ligroin this product was separated into two fractions: form «a» in a prevailing quantity bright light-yellow plates having a m. p. 114°, and form «b» —long yellow needles melting at 144°. Both forms give a positive Bülow reaction. Nitrogen found: form «a»—12.78, 12.77%; form «b»—12.32%; calculated for $C_{12}H_{16}O_2N_2$—12.73%.

A not recrystallized phenylhydrazone was reduced under conditions mentioned above, and leucine was obtained with an 80% yield. After crystallization from water and precipitation with alcohol, the product had a m. p. 292—293° (in a sealed tube). Nitrogen found 10.79, 10.89%; calculated for $C_6H_{13}NO_2$—10.69. The reduction of the «a» form (m. p. 114°) under the same conditions gave leucine with a theoretical yield.

P h e n y l a l a n i n e (in collaboration with E. V. Vinogradova). The benzylacetoacetic ester had the following properties: b. p. 133.5—134°/2 mm; $n_D^{18}=1.5009$; $d_4^{18}=1.0666$; $MR=60.80$; calculated for the ketoform 60.30; for the enolic one 61.34 (without the exaltation). Through coupling with phenyldiazotate, hydrolysis of the coupling product and acidification, the phenylhydrazone of phenylpyruvic acid was obtained. Yield—68% of the theoretical amount. After crystallization from alcohol, quite in agreement with data found in the literature([6]), the product had a m. p. 160° and gave with concentrated sulphuric acid and potassium bichromate a red-violet coloration.

Nitrogen found: 11.07, 10.96%; calculated for $C_{15}H_{14}O_2N_2$—11.05%.

Its reduction unter the above conditions gave phenylalanine with a theoretical yield. After crystallization from water and precipitation with alcohol, the product had a m. p. 265° (in a sealed tube), as found in the literature([7]). Nitrogen found 8.48; 8.44%; calculated for $C_9H_{11}NO_2$—8.49%.

Its copper salt was prepared and analyzed. Found: crystallization water 8.28%; copper 14.36%. Calculated for $(C_6H_5.CH_2CHNH_2.COO)_2Cu.2H_2O$, H_2O—8.41%, Cu—14.86%.

A l a n i n e (in collaboration with V. N. Zaitzeva). Methylacetoacetic ester was purified by way of its Na-derivative according to Michael([8]) and distilled three times under reduced pressure. It had the following properties: b. p. 72°/8 mm; $d_4^{20}=0.9941$; $n_D^{20}=1.4185$; $MR=36.57$; calculated for the ketoform 36.19, for the enolic one 37.24 (without the exaltation). After coupling with phenyldiazonium, hydrolysis of the reaction product and acidification, the phenylhydrazone of pyruvic acid was obtained with a yield 37.75% of the theoretical amount. After crystallization from alcohol it melted at 180°. Nitrogen found 15.75, 15.71%; calculated for $C_9H_{10}N_2O_2$—15.73%. With concentrated sulphuric acid and potassium bichromate the product gives a red-violet coloration (Bülow reaction). The reduction of this phenylhydrazone under the above conditions gives alanine. Yield 93% of the theoretical amount.

After crystallization from water and precipitation with alcohol, the product melted at 290° (in a sealed tube). Nitrogen found 15.76%; calculated for $C_3H_7NO_2$—15.73%.

Its copper salt was prepared and analyzed. Found: H_2O—7.29%; Cu—24.43%; calculated for $(CH_3.CHNH_2.COO)_2$ $Cu.H_2O$: H_2O—6.99%; Cu—24.68%.

The coupling of alkylacetoacetic esters with aromatic diazocompounds, in particular with phenyldiazotate, with a consequent hydrolysis is a sufficiently general and simple method for the preparation of phenylhydrazones of α-ketoacids. The reduction of these phenylhydrazones under the conditions described give α-aminoacids with an almost theoretical yield.

The availability, thanks to this method, of the phenylhydrazones of α-ketoacids which can be easily and completely reduced into α-aminoacids, makes it possible to consider this procedure which is conducted under mild conditions as a new, comparatively simple general method for the synthesis of α-aminoacids.

Further investigations along this line are in progress.

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CHEMISTRY

SYNTHESIS OF PHENYLALANINE FROM BENZYLMALONIC AND BENZYLCYANOACETIC ESTERS THROUGH THE PHENYLHYDRAZONE OF PHENYLPYRUVIC ACID. II

By V. FEOFILAKTOV and E. VINOGRADOVA

(Communicated by N. D. Zelinsky, Member of the Academy, 25. VI. 1939)

The easy preparation with good yields of the phenylhydrazones of the alkylpyruvic acids by means of alkylacetoacetic esters and the reduction of these phenylhydrazones to α-aminoacids, a process which in many cases proceeds quantitatively (see Communication I), makes these phenylhydrazones particularly interesting, especially from the point of view of using them for the synthesis of α-aminoacids.

In order to widen and generalize the method of the practical preparation of these phenylhydrazones we have carried out experiments on the preparation of some of these products, particularly of the phenylhydrazone of phenylpyruvic acid, starting from alkylmalonic and alkylcyanoacetic esters.

Certain indications concerning this problem may be found in the literature. Thus, Favrel[1] has stated that through the action of phenyldiazonium upon methylmalonic and ethylmalonic esters in an acetic acid solution, the phenylhydrazones of pyruvic and of methylpyruvic acid are obtained. The same author[2] has observed the formation of the phenylhydrazone of the nitrile of pyruvic acid as a result of the reaction of the methyl ester of methylcyanoacetic acid with diazobenzene, both in an aqueous alkali and in an acetic acid solution. The author mentioned no yields, the work having a purely qualitative character with the purpose of establishing the nature of the compounds formed—mixed azocompounds or phenylhydrazones.

Such a procedure for the synthesis of α-aminoacids is of considerable interest, because it diminishes noticeably the number of stages of the synthesis. Thus, for instance, in the case of alkylmalonic ester, instead of the usual scheme

$$RCH(COOC_2H_5)_2 \rightarrow RCH(COOH)_2 \rightarrow RCBr(COOH)_2 \rightarrow RCHBrCOOH \rightarrow RCHNH_2COOH$$

the synthesis could be carried out according to such a scheme:

$$RCH(COOC_2H_5)_2 \rightarrow \begin{matrix} RC\cdot COOH \\ \| \\ N\cdot NHC_6H_5 \end{matrix} \rightarrow RCH\cdot NH_2\cdot COOH.$$

The experiment confirmed this assumption to a great extent.

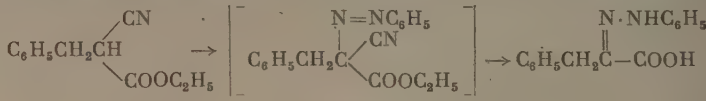
Thus, through the coupling of potassium phenyldiazotate with benzylmalonic ester the phenylhydrazone of phenylpyruvic acid has been obtained with a yield of about 60% of the theoretical amount:

$$C_6H_5CH_2CH(COOC_2H_5)_2 \rightarrow \left[\begin{matrix} N{=}NC_6H_5 \\ | \\ C_6H_5CH_2C(COOC_2H_5)_2 \end{matrix}\right] \rightarrow \begin{matrix} N\cdot NHC_6H_5 \\ \| \\ C_6H_5CH_2C-COOH \end{matrix}$$

Benzylmalonic ester, used as the initial product, had the following properties: b. p. 162°/9.5 mm; $n_D^{20}=1.4871$; $d_4^{20}=1.0763$; $MR=66.85$ (calculated 66.56).

The coupling was carried out through the addition of the ester to an aqueous solution of potassium phenyldiazotate, the reaction mixture being cooled with ice water. The reaction product, an oily liquid coloured red-brown and having presumably the structure II, was separated, hydrolyzed with an alcoholic-aqueous alkali solution, and after the elimination of the alcohol acidified with hydrochloric acid. The phenylhydrazone (III) separated as an oil that solidified rapidly. After crystallization from 80% acetic acid, the phenylhydrazone forms light brown crystals, m. p. 160—161°. This coincides with data found in the literature[3]. Nitrogen found 10.90, 10.86%; calculated 10.05%. Being mixed with a preparation obtained from benzylacetoacetic ester (see Communication I), this product showed no depression of the melting point. With concentrated sulphuric acid and potassium bichromate, the mixture assumed a red violet colour, typical for phenylhydrazones. This colour in a few minutes turned into a brownish one (Bülow reaction).

Through the coupling under similar conditions of potassium diazotate with benzylcyanoacetic ester the same phenylhydrazone of phenylpyruvic acid was obtained. The yield was 30% of the theoretical amount.



I II III

The initial product, benzylcyanoacetic ester, had the following properties: b. p. 132—134°/2 mm; $n_D^{19.6}=1.5057$; $d_4^{19.4}=1.0859$; $MR=55.54$ (calculated 55.49). The product of the coupling, a red-brown oil having presumably the structure II, was separated and immediately hydrolyzed by boiling with an alcoholic-aqueous alkali solution. After acidification there separated a phenylhydrazone similar with the one obtained previously, as judging from the m. p. 160—161°, a mixture test and by the results of the analysis. Nitrogen found—11.07, 11.02%; calculated 11.05%.

And finally, under the same conditions, but starting from sec.-butylmalonic ester, we have obtained, although as yet with poor yields, the phenylhydrazone of methyl-ethylpyruvic acid similar with the one obtained previously from sec.-butylacetoacetic ester (see Communication I).

Thus, taking into consideration that the coupling of phenyldiazotate with alkylacetoacetic esters, as it follows from our Communication I, is a sufficiently general method for the practical preparation of the phenylhydrazones of α-ketoacids and from them α-aminoacids, the same hydrazones can be obtained apparently with practically acceptable yields from alkylmalonic and alkylacetoacetic acids. It follows that the latter esters can be used as the initial products for the synthesis of α-aminoacids.

Investigations in the direction of a further generalization of this method are being continued by us.

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CHEMISTRY

ACTION OF BROMINE ON SODIUM ETHYLATE

By L. N. PARFENTYEV and M. M. ABRAMOV

(Communicated by N. D. Zelinsky, Member of the Academy, 4. VII. 1939)

Publications by Seel and Salzmann(1) and Barth(2) mention the fact that when sodium ethylate is acted upon with bromine a number of products are obtained, such as aldehyde, ethyl bromide, bromal, acetic acid. An analogous work was done by Lagerev(3) at the Laboratory of Organic Chemistry of the Samarkand University. He acted on dry sodium ethylate with bromine, and showed that diacetyl is formed among the products of this reaction. All the authors mentioned studied this process by acting with bromine immediately on dry sodium ethylate, and for this reason their experiments were performed under very difficult conditions which were the cause of such a great variety of products being formed. We took interest in the reaction between bromine and an alcoholate in some medium. For the primary experimental solution of this problem we chose ether as the medium.

Having prepared dry sodium ethylate dust after the expansion method we treated it with bromine in dry ether. The reaction product formed was mainly acetoethyl ether, with a yield of 58% towards theory.

In this work we were successful in directing the reaction along a definite line and producing quite a definite substance with a big yield. We find it more difficult to represent the mechanism of the reaction. If only it can be considered that the first stage of the reaction is ethyl peroxide which may have formed according to the reaction

$$2CH_3CH_2ONa + 2Br \rightarrow CH_3 \cdot CH_2 \cdot O \cdot O \cdot CH_2 \cdot CH_3 + 2NaBr$$

and if the instability of the latter to reducers is taken into account, the resulting phase of the process should be the dehydration of ethyl peroxide, which leads to the formation of acetoethyl ether:

$$\begin{matrix} CH_3 \cdot CH_2 \cdot O \cdot O \cdot CH_2 \cdot CH_3 \\ CH_3 \cdot CH_2 \cdot O \cdot O \cdot CH_2 \cdot CH_3 \end{matrix} \rightarrow CH_3 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_3$$
$$CH_3 \cdot COOCH_2 \cdot CH_3 + H_2O.$$

Action of Bromine on Sodium Ethylate in Dry Ether. Dry alcoholate dust was prepared from 12 g of sodium ethylate in a round-bottomed flask (after the method of A. E. Arbusov). The flask was joined to a reflux condenser by means of a horned adapter and then bromine (40 g) was slowly added through a drop funnel. Cooling with ice water and stirring strongly in dry ether (200 cm³) as the medium was being done all the time. After finally adding the bromine during an hour's time, the flask was heated over a water bath, and then the contents of the flask were left

standing for 12 hours. Then the liquid part was decanted from the sodium bromide precipitate and the latter was treated with dry ether three times. The ether was distilled off from the solution containing the reaction products, after which there were 14 g still left in the flask. The rest of the liquid was distilled under usual conditions, and the main part collected at 710 mm between 60 and 75° was 12 g in quantity. After being distilled fractionally three times from a flask with a small polished deflegmator there were 9.7 g of pure substance left. This was a liquid with a boiling point of 72—73°C at 710 mm with the characteristic odour of acetoethyl ether mixed with alcohol and ether in all proportions.

A mixed test with pure acetoethyl ether did not show a decrease in the boiling point. When saponified with sodium hydroxide a salt is produced which decomposes under the action of sulphuric acid giving off a strong odour of acetic acid, which shows without doubt that we really had acetoethyl ether. In specific weight, refraction and other properties the ether is identical with that produced under the action of concentrated sulphuric acid on ethyl alcohol, i. e. the boiling point is 72—73° at 710 mm; $n_D^{18.5}=0.9030$; $d_4^{20}=1.38048$.

Analysis. 0.1256 g subst.: 0.2420 g CO_2; 0.1028 g H_2O. Found: C—53.26%; H—9.07%. Calculated: C—53.54%; H—9.09%.

Conclusions. When dry sodium is acted upon with bromine in ether solution, the reaction goes in the direction of the formation of acetoethyl ether.

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CHEMISTRY

CONTRIBUTION TO THE STUDY OF KETONES. I. CONDENSATION OF KETONES WITH CYANOACETIC ACID

By M. M. SHEMIAKIN and D. M. TRACHTENBERG

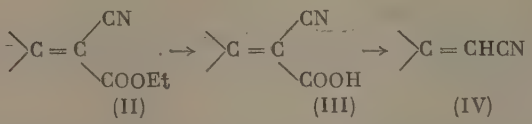
(Communicated by N. D. Zelinsky, Member of the Academy, 4. VII. 1939)

As is well known, ketones in comparison with aldehydes have in a much lesser degree the capacity to condense with compounds containing «an active methylene group». In the case of the majority of aldehydes that type of reaction proceeds very readily, this being widely used for the most varied syntheses of organic compounds, whereas ketones, on the contrary, in the majority of cases react according to scheme (I) only with difficulty

$$>C=O + H_2C< \xrightarrow{-H_2O} >C=C< \qquad (I)$$

Thus, the condensation of ketones with ethyl malonate requires much harder conditions (heating to 100—110° for 60—80 hours in the presence of acetic anhydride and zinc chloride or of the double salt of aniline and zinc chloride). The condensation of the most active ketones, for instance of acetone(1) or in the alicyclic series of cyclopentanone or cyclohexanone (2), gives 30—50% yields, but already in the case of methyl-ethyl ketone under the same conditions the yield does not exceed 19%(3). The condensation of ketones with malonic acid(4) can be carried out under milder conditions—heating at 100° for 2 hours (in a pyridine solution in the presence of piperidine), but in this case too satisfactory yields (35—60%) are obtained only in the case of a few ketones (acetone, diethylketone), and already the condensation of cyclohexanone, for instance, gives a 5% yield only. The condensation of ketones with esters of cyanoacetic acid proceeds more readily and under certain conditions with better yields. The condensation in the presence of metallic sodium is accompanied usually by a series of secondary processes(5) and even if the reaction proceeds according to scheme(I), the yields are poor [in case of cyclohexanone 13%(6)]. The condensation in the presence of an alcoholic solution of ammonium hydroxide or of fatty primary amines likewise does not proceed according to scheme (I), but leads to the formation of β, β-disubstituted α,α'-dicyanocyclic imids of glutaric acid(7). The best catalysts for the condensation of ketones with esters of cyanoacetic acid were found to be piperidine(8) and, as shown recently by Cope(9), the salts of amines and especially acetamide in an acetic acid solution. According to Cope (l. c.) the yields of the condensation products obtained according to scheme (I) in the case of the majority of fatty and alicyclic ketones amount to 70—90%, with the exception of acetone and methyl-ethyl ketone when the yields do not exceed 30—40%.

If therefore the last method is not applied, it is only a few most simple ketones that can be condensed according to scheme (I). Different condensing agents lead often either to the appearance of side processes, or to a considerable charring of the reaction products, and this restricts still more the possibility of applying these methods. As to the interaction of ketones with ethyl cyanoacetate under the conditions developed by Cope (l. c.), it must be said that though in this case the condensation proceeds with good yields, yet the products obtained (of the general formula II) have only a limited importance. The most interesting possibility from the synthetical point of view consists in the transformation of these products by way of nitriloacids (III) into nitriles (IV), but it is not easy to carry this out, chiefly because of the difficulty to hydrolyze the cyanoesters (II).



(II) (III) (IV)

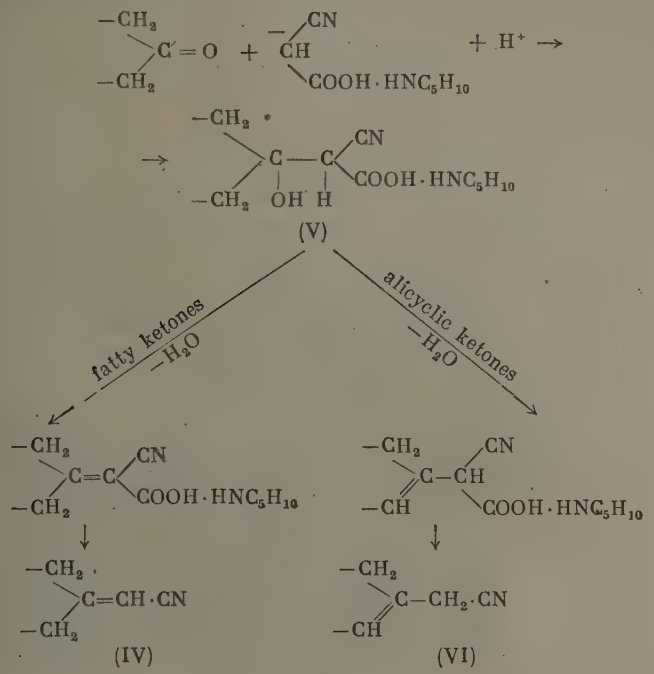
Thus, for instance, according to Ingold and Thorpe[10] α-hydrindilidencyanoacetate is hydrolyzed into the corresponding acid with yields amounting to 30%; and according to Birch and Cone[11] hexylidencyanoacetate is being transformed into the corresponding nitrile with such poor yields, that in general this method cannot be recommended for the preparation of the latter.

The difficulty of obtaining by this way nitriles of type (IV) which we needed for certain purposes, made us seek for other possibilities of their synthesis. A successfull solution of this problem proved to be the condensation of ketones not with the esters of cyanoacetic acid, but with the acid itself under specified conditions. Only a few condensations of this type are described in the literature, for instance, those of acetone, acetophenone[12] and cyclohexanone[6] in the presence of piperidine or of its hydrochloride; the authors stated invariably the formation of the corresponding nitriloacids (of the general type III), but did not mention their yields. In contrast with these investigations we carried out the condensation of different ketones with a considerable excess both of cyanoacetic acid and of piperidine (2—3 times the necessary amount). With such amounts of the reagents, a reaction temperature of 100—115° C and the duration of the reaction about 2 hours, alicyclic ketones (cyclopentanone, cyclohexanone, α-hydrindone) as well as fatty ones (acetone, methyl-ethyl-ketone) are converted directly into the corresponding nitriles, the yield being 70—90%. Thus, under rather mild conditions the ketones are not only easily condensed with cyanoacetic acid giving good yields, but at the same time a complete decarboxylation of the intermediate nitriloacid takes place. At the end of the reaction we invariably found only nitriles, but no nitriloacids*. It should be noted that while fatty ketones form nitriles of the general formula (IV), all the alicyclic ketones that we investigated were converted not into nitriles with a semicyclic double bond, but into nitriles having a double bond in the ring (VI).

In agreement with modern views upon the condensation processes of carbonyl compounds with compounds containing «active methylene groups» ([9],[13]),

* Such an easy decarboxylation of nitriloacids under conditions of our process may possibly be ascribed to the presence of a considerable excess of piperidine. Dutt [4] points out that alkylidenmalonic acids in a pyridine solution, in the presence of piperidine, are readily and rapidly decarboxylated to the corresponding monocarboxylic acids already at a temperature of 100°.

we propose the following scheme for the condensation process of ketones with cyanoacetic acid:



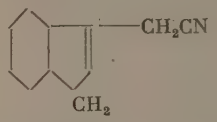
The condensation reaction should proceed first and is followed by decarboxylation. This is supported by the fact that when cyanoacetic acid was heated with piperidine (the same proportions being used) in the absence of a ketone, we could not prove the formation of acetonitrile*. As was mentioned above, the best catalysts for condensations of this kind are not the free amines, but their salts. According to Cope [9] as well as to other authors [13,14], the salts of amines catalyze simultaneously the ionization process of the methylene component as well as the dehydration of the intermediate aldol condensation product (V). Under the conditions of our experiment the part of such a catalyst is being played by the piperidine salt of cyanoacetic acid. The fact that a considerable excess of the latter must be taken in order to obtain good yields of the nitrile, support the point of view that this salt is actually a catalyst of this process.

Whereas fatty and alicyclic ketones react with cyanoacetic acid with the formation of the corresponding nitriles and give such good yields that this procedure may be recommended as a practical method for the synthesis of the latter, aromatic and fatty-aromatic ketones (at least those investigated by us—benzophenone and acetophenone) do not react at all with cyanoacetic acid under the conditions specified above.

All the nitriles that we prepared using this method had properties which coincided with those of the corresponding nitriles described in the literature.

* As at present no sufficient data are available concerning the fact whether dehydration precedes the decarboxylation process or not, in that part the proposed scheme is somewhat arbitrary, though certain reasons give us the possibility to decide in favour of such an order of the process.

Through their hydrolysis the esters were obtained and then the acids with constants corresponding as well to those found in the literature. Hydrindenylacetonitrile obtained by us had a m. p. 68—70° C. Ingold and Thorpe [10] for the same nitrile give a m. p. 18° C. These authors attributed to the compound obtained by them the following structure (VIII):



(VIII)

but without supporting it by any fact. The oxidation results obtained with our nitrile (no α-hydrindone was found among the oxidation products) as well as its incapability to add bromine, gives us the possibility to ascribe to this compound the structure expressed by the formula (VIII). Probably, the compound described by Ingold and Thorpe (l. c.) is its isomeride with a semicyclic double bond—hydrindilidenacetonitrile.

Condensation of Cyclopentanone with Cyanoacetic Acid. To 5 g of the ketone and 7.5 g of cyanoacetic acid were added through the reflux condenser 7.5 g of piperidine. A considerable heat effect took place. The mixture was heated to 100—105° C for two hours. Ether was added and the ether solution was subsequently extracted with diluted sulphuric acid (to an acidic reaction of the washings), with a sodium carbonate solution (to an alkali solution of the washings), with water, and dried over sodium sulphate. After the distillation of the ether, the residual liquid was distilled under reduced pressure, the fraction 124—125°/100 mm being collected. The yield of cyclopentenylacetonitrile was 5.75 g (90% of the theoretical amount). The properties of the nitrile corresponded to those found in the literature [8]. By its hydrolysis under conditions specified by Hardner and Haworth [8] cyclopentenylacetic acid, m. p. 49—51°C [15], was obtained.

Condensation of Cyclohexanone with Cyanoacetic Acid. 5 g of the ketone, 9.9 g of cyanoacetic acid and 9.9 g of piperidine were mixed. The reaction and the isolation of the nitrile were carried out as described above. The yield of the cyclohexenylacetonitrile was 4.5 g (73%), b. p. 140—142°/ 85 mm. The properties of the nitrile corresponded to those described in the literature [8]. By its hydrolysis under conditions specified by Hardner and Haworth [16] cyclohexenylacetic acid, b. p. 138—140°/ 11 mm [17], was obtained.

Condensation of Acetone with Cyanoacetic Acid. 5 g of the ketone, 16.5 g of cyanoacetic acid and 22 cm³ of piperidine were heated for two hours at 110—115° C. The nitrile was isolated as described above*. The yield of the nitrile of β,β-dimethylacrilic acid was 5 g (71%), b. p. 140—142° C. The properties of the nitrile corresponded to those described in the literature [18]. By its hydrolysis under conditions specified by Hardner and Haworth (l. c.) β,β-dimethylacrilic acid, b. p. 192—194° C [19], was obtained.

Condensation of Methyl-Ethyl-Ketone with Cyanoacetic Acid. To 5 g of the ketone and 13 g of cyanoacetic acid were added 16 cm³ of piperidine. The reaction and the isolation of the nitrile were carried out as described above for acetone*. The yield of the nitrile of β-methyl-β-ethylacrilic acid, b. p. 88—90° C/75 mm, or 158—160° C/760 mm, was 4.7 g (70%). The properties of the nitrile corresponded

* As the nitrile is well soluble in water, minimum amounts of the acid (25%) and the sodium carbonate solution (10%) are being used for the extraction of the ether solution.

to those described previously ([16]). By its hydrolysis under conditions specified by Hardner and Haworth (l. c.) β-methyl-β-ethylacrilic acid, b. p. 205—208° ([16]), was obtained.

Condensation of α-Hydrindone with Cyanoacetic Acid. 12. 5 g of the ketone, 25 g of cyanoacetic acid and 16 g of piperidine were heated for two hours at 110—115°. The nitrile was isolated as usual and distilled under reduced pressure. The unchanged α-hydrindone was distilled at 125—128°/17 mm; α-hydrindenylacetonitrile distilled at 126—128°/2 mm and rapidly crystallized. The yield was 6.7 g (70%). After crystallization from 50% alcohol the crystals melted at 68—70° C. The products did not decolourize bromine in ether solution.

Analysis: found,%:N—8.83; calculated for $C_{11}H_9N$,%:N—9.03.

Oxidation of α-Hydrindenylacetonitrile. To 0.4 g of the nitrile and 10 cm³ of a 1% solution of sodium hydroxide a 5% solution of potassium permanganate was gradually added with efficient stirring. The latter was being added only after the discoloration of the previous portion. In all 70 cm³ were used during a run of about 11 hours. The excess of the permanganate was eliminated by the addition of alcohol. Both the precipitate and the filtrate were extracted with ether. No α-hydrindone was found in the ether extract (negative reaction with semicarbazide).

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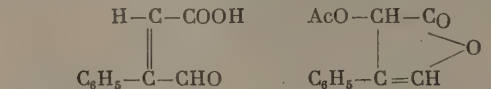
CHEMISTRY

CONTRIBUTION TO THE STUDY OF ALDEHYDOACIDS AND ALDOENOLLACTONES. IV. SPECIFIC TRANSFORMATIONS OF CERTAIN ALDEHYDOACIDS AND γ-ALDOENOLLACTONES IN AN ALKALI MEDIUM

By M. M. SHEMIAKIN

(Communicated by N. D. Zelinsky, Member of the Academy, 4. VII. 1939)

We have shown in a previous paper (1) that one of the interesting particularities of certain aldehydoacids and γ-aldoenollactones consisted in their peculiar behaviour towards alkalis. Thus, β-phenyl-β-formylacrylic acid (I) or its ethyl ester as well as α-acetoxy-β-phenyl-γ-aldoenollactone (II) [all of them have been formerly synthetized by us (2)]

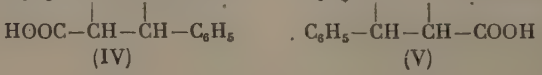


(I) (II)

when heated with dilute solutions of alkalis undergo a series of far going transformations, the final result of which is a dicarboxylic acid, the same for all cases, a dimeride of cinnamic acid of the empirical formula $C_{18}H_{16}O_4$ (III). The peculiarity of these transformations and the astonishing readiness with which they proceed [for particulars see Communication III (1)] impelled us to investigate this process in detail and first of all to confirm those assumptions that we had expressed concerning the nature of the final product of these transformations—the dicarboxylic acid (III), the more that this acid is of no less an interest than the process of its formation.

Preliminary data that we had at hand at the time made us suppose that this acid belonged to the series of diphenylcyclobutanedicarboxylic acids.

The series of diphenylcyclobutanedicarboxylic acids has attracted in the past and is attracting at present the attention of many scientists, because of its considerable interest from the point of view of stereochemistry. On the base of stereochemical conceptions it is possible to predict the possibility of the existence of 11 spatially isomeric forms, among which 4 can be additionally split into optically active forms. The reason for such a variety of isomerides is the simultaneous existence both of the cis-, trans- and of the optical isomerism. The large number of studies devoted to these acids was called forth to a great extent by the fact that they were used as one of the objects which served to confirm the validity of stereochemical conceptions. Usually the diphenylcyclobutanedicarboxylic acids are subdivided into two series—the truxillic (IV) and the truxinic (V) acids.



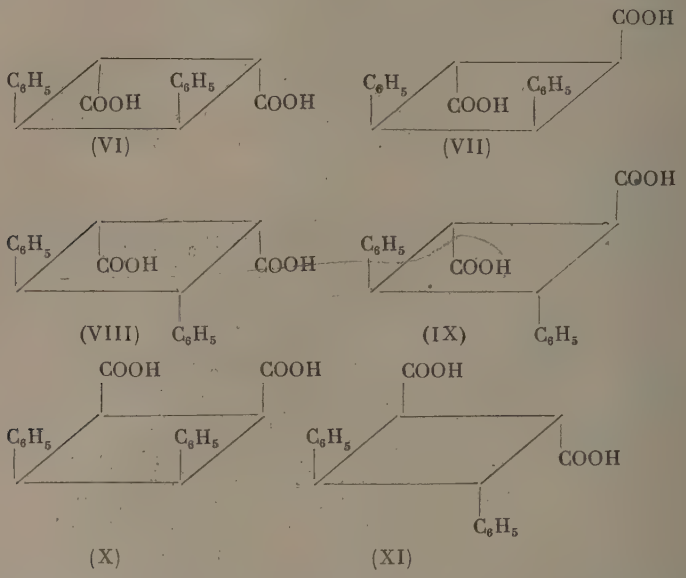
(IV) (V)

Five of them belong to the truxillic acids. All of them are known and their configuration has been determined quite definitely mainly thanks to Stoermer. The remaining six diphenylcyclobutanedicarboxylic acids belong to the truxinic acids, out of which, notwithstanding numerous endeavours, mainly by Stoermer, only four have been found. The acid obtained by us (III) and its methyl ester corresponded by their melting point to neither of the diphenylcyclobutanedicarboxylic acids known in the literature. That is the reason why already in our former paper [1] we made the assumption that this acid might be one of the two truxinic acids that as yet have not been obtained. The considerations mentioned above impelled us to investigate in detail the nature of this acid. The results of this investigation are reported in the present paper.

The acid (III), m. p. 196°, according to data of the ultimate analysis, of titration and of the determination of the molecular weight proved to be a dicarboxylic acid of the empirical formula $C_{18}H_{16}O_4$ [see Communication III[1]]. The acid was characterized by many new derivatives, the constants and properties of which did not coincide with those of the corresponding derivatives of all the known truxinic acids. The easiest way to prove that our acid was actually a truxinic acid seemed to us its transformation into one of the known acids. The possibility of the isomerization of certain truxinic acids into other ones has been known on many examples [3]. That is the reason why we undertook a few attempts in this direction with the hope to solve the problem concerning the nature of our acid. Actually, when its methyl ester was heated during one hour at 260°, the latter was completely isomerized into a mixture of esters of two new acids. After the hydrolysis of the esters the acids could be separated through fractional crystallization from glacial acetic acid. The melting points of the two acids obtained in this way were 211 and 245°. The melting point of the first of these acids coincided with the melting point of two known truxinic acids, β and neo. Both these acids have the same melting point 209—210° [4]. The most sharp difference existing between the two consists in the fact that β-truxinic acid which is a cis-dicarboxylic acid (VI), forms easily the corresponding anhydride, melting at 116°[5], and the neo-acid (VII), as a transdicarboxylic acid, does not have its own anhydride, but is converted under much more severe conditions into the anhydride of the β-acid [6]. Under the conditions described for the preparation of the anhydride of the β-acid [5], the acid with m. p. 211° gave an anhydride which melted at 116°, that is, at the same temperature as the anhydride of the β-acid. This fact proved the identity of the two acids. At the same time it was established that the acid with m. p. 196° found by us belonged to the series of truxinic acids and was one of the two diphenylcyclobutanedicarboxylic acids which until now have remained unknown.

The second acid (m. p. 245° C) that is obtained simultaneously with the β-truxinic acid and which is its isomeride, has a melting point very near that of the ς-truxinic acid (VIII), though it does not coincide with the m. p. of the latter—245 and 239° [7]. The properties of its methyl ester and chloride did not coincide by far with those of the analogous derivatives of ς-truxinic acid [for the methyl esters correspondingly 133 and 116° [7] and for the chlorides 144 and 150° [7]]. Another fact speaking against the identity of these two acids was the transformation of the acid with m. p. 196° into an acid with m. p. 245° under conditions (heating with concentrated hydrochloric acid at 180—190°) when ς-truxinic acid cannot exist, but should be transformed into the isomeric δ-truxinic acid (IX) with m. p. 175° [7]. It follows that the acid with m. p. 245° was, probably, the last of the unknown, up to the present, truxinic acids.

The configurations of the four previously known truxinic acids have been established with sufficient definitiveness mainly by Stoermer (l. c.): for the β-acid the formula (VI), for the neo—(VII); for ς—(VIII), for δ—(IX). Therefore for the last two acids found by us only the formulae (X) and (XI) remain.



The question as to what acid should be ascribed the one or the other configuration is not to be answered without further investigation which is now under way.

At long last, it is necessary to point out certain particulars of the acid melting at 196° C. As was already mentioned before (1), the carboxyl groups of this acid differ unusually sharply from each other in their degree of dissociation. When titrated directly with a 0.1 *N* solution of sodium hydroxide in the presence of phenolphtalein, the neutralization of only one carboxyl group and the formation of a monosodium salt takes place. The second carboxyl group can be neutralized only with an excess of alkali (1), but not with sodium carbonate. Consequently, the degree of its dissociation is weaker than that of carbonic acid. This difference between the two carboxyl groups is expressed not only in their degree of dissociation, but in the properties of certain derivatives of this acid as well. Thus, differently from other truxinic acids, this acid has two methyl esters. One of them (m. p. 196°) was described previously (1), and the other has a m. p. 183° and is obtained when the acid is refluxed in an alcohol solution in the presence of sulphuric acid. Both esters are insoluble in alkalis even when heated. Whereas the second ester at a temperature of 260° is isomerized into a mixture of esters of two other truxinic acids (see above), the first ester under those conditions undergoes no changes. When the acid was boiled with thionyl chloride, it was not the dichloride, as in the case of other truxinic acids, that formed, but the monochloride. The latter, though having a free carboxyl group, was insoluble in a cold alkali solution, and formed with aniline a monoanilide also insoluble in alkalis. Such a peculiar behaviour of this acid as well as of certain of its derivatives is probably connected with particularities of the spatial structure of this acid. Our considerations

on the subject will not be expressed until after some additional studies have been made and the configuration of the two truxinic acids found definitely established.

The author wishes to express his sincere thanks to Prof. V. M. Rodionov for his valuable suggestions that were of great help in the present investigation.

Truxinic Acid, m. p. 196°, and its Derivatives. The preparation of the acid was described in a previous paper (1). After two crystallizations from ether the acid had a m. p. 196°.

Methyl Ester, m. p. 196°. Its preparation was described in a previous paper (1). Insoluble in alkalis in the cold. Dissolved only after boiling for 5—10 min. with a 5% solution of sodium hydroxide.

Analysis: Found,%: C—73.68; H—5.83.

Calculated for $C_{20}H_{20}O_4$, %: C—74.04; H—6.22.

Methyl Ester, m. p. 183°. Two grams of the acid were dissolved in 30 cm³ of boiling methyl alcohol, 2 cm³ of concentrated sulphuric acid were added and the mixture refluxed for 5 min. A precipitate separated and was filtered off. Yield 1.9 g. After crystallization from ethyl alcohol the product melted at 183°.

Analysis: Found, %: C—74.17; H—5.95.

Calculated for $C_{20}H_{20}O_4$,%: C—74.04; H—6.22.

Monochloride. 0.5 g of the acid and 2 cm³ of thionyl chloride were refluxed for 30 min. The thionyl chloride was distilled and the residue crystallized twice from benzene. The yield of the product, m. p. 150°, was 0.35 g. Insoluble in alkalis in the cold, but dissolved rapidly when heated.

Analysis: Found,%: Cl—11.08.

Calculated for $C_{18}H_{15}O_3Cl$, %: Cl—11.28.

Monoanilide. To 0.25 g of the monochloride in 12 cm³ of dry benzene 1 g of aniline in 10 cm³ of dry benzene were added. The precipitate which separated at once was washed with water and crystallized twice from xylene. The yield of the product, m. p. 241°, was 0.25 g.

Analysis: Found, %: N—3.91.

Calculated for $C_{24}H_{21}O_3N$,%: N—3.77.

Isomerization of the Acid, m. p. 196° C. 0.5 g of the acid and 10 cm³ of concentrated hydrochloric acid were heated in a sealed tube during 2 hours at 180—190°. The dark precipitate was crystallized twice, using activated coal, from glacial acetic acid. The yield of the product, m. p. 245°, was 0.1 g.

Analysis: Found, % : C—72.82; H—5.68.

Calculated for $C_{18}H_{16}O_4$, %: C—72.94; H—5.45.

Isomerization of the Methyl Ester, m. p. 183° C. 0.55 g of the ester were heated in a narrow test tube at 260° for 1 hour. The viscous mass was subjected to fractional crystallization and separated into 3 fractions (1st fraction, m. p. 130—133°; 2nd fraction, m. p. 120—123°; 3rd fraction, m. p. 105—107°). Each fraction was hydrolyzed by boiling with concentrated hydrochloric acid for 3—4 hours. The acids obtained through the hydrolysis of the 1st and 3rd fractions were crystallized 2—3 times from glacial acetic acid. From the 1st fraction an acid, m. p. 245°, was obtained which proved to be identical with the one obtained in the former experiment. Poorly soluble in cold acetic acid and well soluble when heated. From the 3rd fraction an acid was obtained which melted at 211°. Rather well soluble in cold acetic acid and very well soluble when heated. The 2nd fraction proved to be a mixture of the two acids and was subjected to fractional crystallization from glacial acetic acid. The yield of the acid,

m. p. 245°, was 0.22 g, and that of the one melting at 211°, 0.12 g. The anhydride of the latter acid was obtained by heating it with acetic anhydride during 20 min. at 110—115°. The acetic anhydride was eliminated under diminished pressure and the residue crystallized from a mixture of benzene and ligroin. M. p. 116°.

Derivatives of the Truxinic Acid, m. p. 245°. Methyl Ester. 0.1 g of the acid was refluxed for 30 min. with 10 cm^3 of methyl alcohol and 0.5 cm^3 of concentrated sulphuric acid. The mixture was diluted with a large amount of water and the precipitate that separated crystallized from alcohol. The yield of the product, m. p. 133°, was 0.08 g. It proved to be identical with the ester which was formed through the isomerization of the ester, m. p. 183° (see above).

Chloride. 0.1 g of the acid was refluxed during 1 hour with 1 cm^3 of thionyl chloride. The excess of the latter was distilled and the residue was crystallized twice from ligroin.

The yield of the product, m. p. 144°, was 0.03 g.

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CHEMISTRY

MECHANISM OF FORMATION AND DEVELOPMENT OF A LATENT PHOTOGRAPHIC IMAGE

By P. D. DANKOV

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§ 1. In spite of the astonishing achievements in the domain of the theory of the formation ([1]) and the development ([2]) of the latent photographic image, the picture of the mechanism of these phenomena still lacks integrity. It has also essential gaps, which leaves one unsatisfied with and even doubtful of the correctness of ideas that are essentially true.

In this study an attempt is made to analyze more thoroughly the mechanism of the formation and development of the latent photographic image. To this purpose it was found necessary to take into account the principle of orientational and dimensional conformity, suggested by the author ([3]), of the processes which develop at the boundary of two phases. At the same time the proposed scheme contained the idea of the electrocrystallizational nature of the metal's precipitation during reduction processes ([4]).

§ 2. The phenomenon of the formation of the latent photographic image develops during the photochemical process ([5,6]):

$$Ag^+Br^- + h\nu = Ag^+ + Br\uparrow + \Theta \qquad (1)$$

$$Ag^+ + \Theta = Ag \qquad (2)$$

This scheme is in full accord with the experimental material of Koch and Kreiss and Hartung ([7]) and especially that of Paul and collaborators ([8]) and Savostianova ([9]). In the works of the latter it was very clearly shown that the latent photographic image consists of crystallization centers not in an atomic, but in a colloidal stage of dispersion. As may be seen from the following, in order to attain such a state there is no necessity of considerable translocation of the silver atoms for the formation of comparatively large particles. At the same time it was found that the equation (2) given above should be somewhat modified.

From the point of view of the orientational conformity principle the process

$$\text{crystal}\,[Ag^+\,Br^-] + h\nu = \text{crystal}\,[Ag] + Br\uparrow$$

should go on in that most simple direction which ensures a minimum change in the orientation of the silver atoms (ions). The principle of dimensional conformity postulates minimum translocation of the atoms during the process. For this case both of them are fulfilled in extraordinarily perfect form. Fig. 1 shows that the space lattice of silver bromide can transform into the silver lattice without any change in the orientation of the metal atoms, and

the complex of cube planes $\{100\}$ in the $[Ag^+Br^-]$ lattice will correspond to the octohedron (110) and cube (001) planes in the [Ag] lattice. At the same time, according to the principle of dimensional conformity, the distances between the silver atoms in the cube planes (001), which retain their denomination even after the silver bromide has turned into the metal, do not change at all after bromine has been removed from the crystalline lattice. The latter can be checked by simple calculation which shows that the dia-

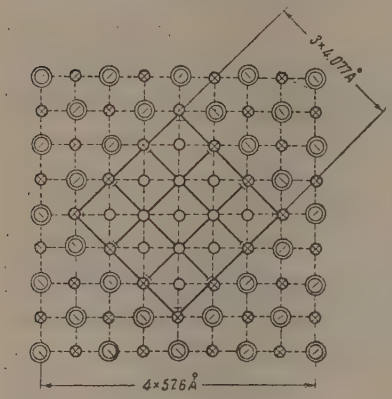

Fig. 1. Space lattice of silver bromide with alternating ions of silver and bromine. Silver ions as connected by solid lines form plane systems with their parameters corresponding to the crystalline lattice of the metallic silver. The three-dimensional figure obtained by the combination of such plane lattices fails to correspond perfectly to the elementary cell, since its parameter in the direction of the vertical axis is 26% greater.

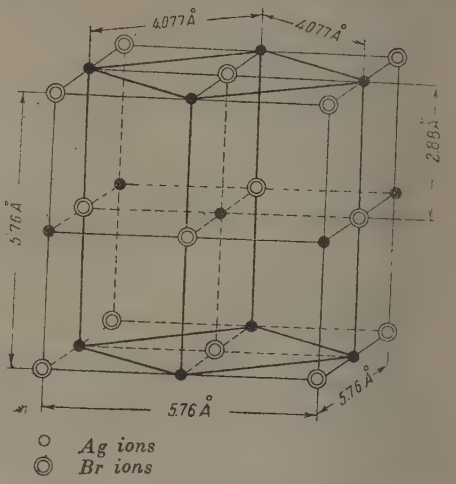

Fig. 2. Crystalline plane (100) of crystal [AgBr]. In the middle the bromine atoms are substituted with silver atoms which arrived from more deeply located neighbouring places of the crystal. This system of atoms forms a plane metallic nucleus. The extreme atoms of the latter are also a part of the crystal [AgBr] and can be referred to both. Take the whole of them for a positive outer covering of the doubre layer in the «moving» cathode and assume that the center of the nucleus is a reducing electrode taking up electrons, and it will be obvious that the system is a special kind of element liable to be set in operation by the movement of the neighbouring Br ions from the crystal to the liquid solution (perpendicular to the plane of the drawing), where the crystal [AgBr] is immersed after its exposure to light.

gonal of the cube plane in the crystalline lattice of silver ($a=4.077$ Å), which is equal to $\sqrt{2\,(4.077)^2} = 5.76$ Å, equals the constant of the silver bromide lattice with accuracy to the second figure after the decimal point ($a_{AgBr}=5.76$ Å). In order that the plane (001) entirely identical to the cube plane (001) in the metal nucleus may form, it is necessary that the silver atom shift upwards from the nearest lower plane (001), from which the bromine atoms have also been removed through the photochemical act. It is clear that in leaving the crystalline lattice, the bromine atom leaves an electron under the «control» not of only one of its neighbours, but of a host of them, which are already a system with the potential barriers for the transition of the electron noticeably lowered and with a large number of electron energy levels ([10]). Therefore the second equation written above should be made

more precise so that the immediate transformation of the crystal of Ag^+ ions into the metallic crystal should be represented:

$$[Ag^+] + \Theta \rightarrow [Ag].$$

Of course, this formation is some transitional stage towards the true metal lattice, characteristic of massive metals. But it already possesses a number of characteristic features of the metallic state. If the light reaction is deep enough, the quantity of bromine atoms which leave the [AgBr] crystal is so great that the system of plane lattices of metallic silver which forms passes into a state of equilibrium without changing its orientation by means of their shifting on 26% in relation to one another (from 5.76 to 4.077 Å). This process results in a system of silver atoms which is a transitional form, closer to the metallic state. Further increase in the dimensions of such a combination of silver atoms puts them into the real metallic state.

These correlations were applied with less success to the formation of the latent photographic image on silver chloride grains. In this case the principle of dimensional conformity is not satisfied well enough, since the diagonal of the cube plane in the silver nucleus (5.76 Å) is 3.8% greater than the edge of the cubic nucleus of silver chloride ($a = 5.54$ Å). This circumstance has apparently something to do with the difficulty in using silver chloride as photographic material. On the other hand, silver bromide which does not possess this limitation is of high technical value and widely distributed.

A preliminary analysis of the phenomenon taking place in rock-salt (and other alkaline-haloid salts), under the action of a light source of short wave length, e. g. X-rays, and of further transformations in the crystal under the action of heat and light, also gave satisfactory correlations which will be examined in a special paper.

§ 3. Turning to the problem of the development of the latent photographic image, it should be emphasized in accordance with Rabinovitch ([11]) that the process goes on right on the boundary [Ag]/[AgBr].

However, the necessity of predominant absorption of the developer on this boundary, as mentioned in the works of Rabinovitch ([11]), is not a necessary condition for the progress of this phenomenon.

According to the scheme of the processes of reducing metals from solutions of their salts worked out by me ([4]), the tiny metal crystal which forms in the primary stage of the process is a microscopic electrode, upon which a double process develops: the giving away of electrons by the reducer and the electrocrystallization of the metal. In this the characteristic peculiarity of the metallic bodies, viz. the mobility of the electrons, plays a very great part: it facilitates the possibility of spatial division of the processes of giving and taking electrons between the reacting particles near the metal surface. Indeed, the reducer should give away an electron and the metal ion must take the latter in order that the reduction process should take place. Of course, fortunate collisions between the reacting particles at the same place on the metal surface should take place, but the number of such collisions is small compared to the number of favourable collisions of each particle separating with the metal surface. Therefore the giving and taking of electrons which go on with the help of the metal surface gives a much more considerable effect than the immediate interaction of the particles between each other.

In the case of the silver bromide crystal reacting with the organic reducers used in photography we have a different picture, since a very small number of silver and bromine ions enter into solution, and they can hardly get away from the place where they tore out of the crystal, if reduction can go on. The reduction process does not go on (and if it does begin, it does

so only after a long induction period) if the crystal was not exposed to light. Exposure of the crystal results in the formation of strictly oriented silver particles which are firmly united with the bromide lattice and have more or less clean-cut metallic properties (depending upon the illumination intensity). A metal—bromide boundary forms, and here reduction goes on during development (Fig. 2). The advantages of the boundary metal—bromide as a place for intensive reduction are obvious: a) the reduction material is right next to the boundary; b) the metallic nucleus is in very close contact with this boundary; c) electrons should be given to the metallic ions being reduced easily on the boundary (difficulties may arise during the desorption of bromine ions which do not give away their electrons during development, but leave the surface together with them); d) the metal nuclei can take electrons from the reducer at all the points of the surface of the reduced metal and not only at the boundary, where the large molecules of the reducer hinder the process rather than help it. Thus, the reduction process may be divided into two parts: 1) at the boundary metal—bromide the electrons of the metal pass over to the ions which are being reduced (and perhaps, the new ions are merely admitted to the ion collective which forms the metal nucleus, in the presence of an excess of electrons obtained from the reducer) and 2) electrons are given over from the reducer to the metal all along the free metal surface. Both conditions imply a rapid increase in the rate of reduction, since the metal surface increases with time, and the boundary metal—halogenide becomes wider and deeper.

The introduction of this correction in the theory of developing does not change the thermodynamic proportions which are expressed by means of equation for electrode potentials applied up till now by various authors ([12]). Now these equations will represent not only the thermodynamic conditions of the process, but also their real relation to the electrode phenomena which really take place.

The progress of the developing process as well as the formation of the latent photographic image should satisfy the principles of orientational and dimensional conformity of the Ag and AgBr crystalline lattice, which is in fact observed when the phenomenon is studied more in detail.

§ 4. In connexion with the theory of photographic processes developed in this paper we should touch upon the mechanism of some phenomena which have not found explanation up till now.

Herschel's effect which consists in the weakening or disappearing of the latent photographic image (formed by exposing to white or blue light) when exposed to red light, was a mystery up till now. However, in the light of the theory of orientational and dimensional conformity Herschel's effect becomes clear: if the orientations and silver atom distances corresponding to the halogenide are retained in the plane metal lattices which form the latent photographic image, it is possible that the spaces which were left by the bromine ions be substituted with the bromine ions which are capable of diffusing from the inner or nearest surface sections of silver bromide, untouched by the preliminary exposure to white or blue light. Only those bromine ions can so diffuse within the crystalline lattice, whose energy is greater than a certain value E; the number of such ions is in proportion to the exponential expression $e^{-\frac{E}{kT}}$. Apparently, if the value E is equal to or less than $h\nu'$, where ν' is the frequency of the red light to which the image is exposed, all the ions which accept such quanta will shift into the neighbouring empty places or, in general, into places where their concentration is less.

However, the frequency of the light should not be too high (evidently, less than 6×10^{14}), since exposure to light of high frequency may result in a supplementary photochemical act, this time in the surface layer, and the bromine atom will be expelled from the crystalline lattice instead of being shifted within the latter. The probability of these correlations increases still more, since rays with short wave lengths have a larger absorption coefficient than rays with long wave lengths. The rays of the long-wave-length part of the spectrum, which pass into the crystal more easily, give Herschel's effect comparatively more successfully than rays of short wave length.

Evidently, the phenomenon of solarization is very closely connected with this phenomenon, but we cannot discuss it in this short paper.

§ 5. The explanation of Weigert's effect [13] is no less interesting. Weigert's effect consists in that the photographic layer (after exposure to white light), being exposed to a beam of polarized light (also from the long wave part of the spectrum), shows anisotropy (dichromatism). This phenomenon was characterized by Cherdynzev [14] as a limited development of Herschel's effect which results in a decrease in the dimensions of the particles which make up the latent photographic image. However, such a decrease can take place in one certain direction, but this direction is common to all the grains of the photographic layer. Therefore, for instance, the forms of the particles change from spheric to ellipsoid with the long axis in the same direction for all the particles of the layer. As we know, such a combination of particles is anisotropic in relation to the rays of visible light.

However, in Cherdynzev's work [14] the mechanism of the phenomenon was not studied. From the point of view of the ideas propounded here, Weigert's effect becomes quite comprehensible: bromine ions within the crystalline lattice diffuse not at random, but in definite directions, e. g. in one of the planes at whose intersection we find bromine ions. Excitation with polarized light is in vectorial accordance with the vectorial nature of the exciter. In view of this, according to the scheme described above, the bromine ions shift only in those planes where the amplitude of light oscillations can reach its maximum. In view of this the metallic combination of silver atoms which formed preliminarily is destroyed by bromine atoms which arrived only in those directions that coincide with the plane perpendicular to the plane of light polarization.

§ 6. This study is only in its initial stage of development. In spite of this it gives the answers to many questions of the theory of photographic processes. No doubt, further development of the ideas suggested here will give even more exhaustive results.

At the same time it must be mentioned that the application found for the principles of orientational and dimensional conformity, and also the new scheme of the mechanism of metal reduction in photography, convinces that it is necessary to study other heterogeneous transformations taking place in photochemical phenomena from this same point of view.

§ 7. In concluding we shall briefly summarize the material of this study.

1. We have given a scheme of the formation of the latent photographic image on the basis of the principles of orientational and dimensional conformity and also ideas of the transitional metallic states.

2. We have given a scheme of the mechanism of photographic development from the point of view of the electronic theory of metal reduction and the conformity principles mentioned above.

3. Explanation of Herschel's and Weigert's effects has been given as a corollary following from the theory suggested.

4. We have shown the possibility of applying the theory proposed above to phenomena of transformations in solid bodies under the influence of radiant energy.

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GEOCHEMISTRY

ISOTOPIC COMPOSITION OF WATER FROM SOME RIVERS AND LAKES OF THE USSR

By R. V. TEIS

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In the determination of the relative density of water which is connected with the study of its isotopic composition, a very serious problem is the problem of standard water, relatively to which the density of all other waters is determined. Usually the water from the water-supply of the city where the measurements are being made is taken for standard. Probably, the assumption is made that the isotopic composition of river or lake waters feeding waterworks is the same for different places of the globe. However, in 1936 Morita and Titani (1) have shown that this is not so. These authors have compiled a comparative table of the densities of crystallization waters for the same samples of minerals, measured at different points of the globe (Washington, London, Osaka). A considerable difference in density (2—3γ) was found out, the water from the Osaka water-supply almost always giving the smallest figure.

Besides, Brodsky, Skarre, Dontzova and Slutzkaya (2) have pointed at the possibility of seasonal fluctuations in density depending upon the river flood in spring. The same authors, when determining the density of water from the rivers of mountainous Karachay, found in some cases a low density which they explained by the fact that these rivers were fed with melted water coming from glaciers and snow-peaks.

In another paper Morita and Titani(3) made a comparison of waters from two water-supplies: that of the town of Osaka and that of the city of Cambridge, Massachusetts, USA. They obtained an almost equal density for these two waters. When the same purification methods were applied, the difference in densities of these two waters and the seasonal fluctuations of the density of the Osaka water did not exceed the error of the experiment. Dole (4) showed that the water of that same city of Cambridge had the same density as the water from lake Michigan.

Taking into consideration that in certain cases the existence of fluctuations of the isotopic composition of waters was still observed, it seemed worth while to compare the densities of water samples taken in different points of the USSR.

As a standard for this comparison we took Moscow tap-water, of which some scores of liters were sampled on January 29, 1938, and laid in store with the addition of potassium permanganate. For the purification of the standard as well as of other waters the method described dy Emeleus, James,

King, Pearson, Purcell and Briscoe([5]) was used. This method was compared with the method of purification described by Brodsky, Skarre, Dontzova and Slutzkaya([5]), and by using two modifications for the determination of the density by means of the plunging of a quartz float (the method of floatation temperatures, and that of floatation pressures) we obtained concurring results within the limits of experimental error (Table 1).

Table 1

Sample of water and method of purification	Floatation $t°$ according to Beckmann thermometer (or floatation pressure in mm)	Difference in γ
Method of Floatation Temperatures		
Standard purified by the method of Emeleus and oth.	2.514°C	0
Standard purified by the method of Brodsky and oth.	2.514°C	
Method of Floatation Pressures		
Water from the Dnieper purified by the method of Emeleus and oth.	215.0 mm	0.2
Water from the Dnieper purified by the method of Brodsky and oth.	216.5 mm	

Further measurements were made also by the method of plunging quartz float in its two modifications*. The accuracy of the measurements in the case of both modifications was within the limits of 0.2—0.3 γ. Among the water samples from rivers and lakes of the USSR we selected those which were not taken at the period of spring flood. Waters from several rivers of the European territory of the USSR, of Siberia and Eastern Transbaikal as well as waters from lakes of different character were measured. The results of these measurements are given in Tables 2 and 3. In the majority of cases the figures given in the tables refer to a sample taken at the surface, with the exception of the lakes Baikal and Razval where the depth is given in the notes.

In Table 2 the densities of waters from different rivers are given. As it may be seen from the table, all the densities of these waters are alike and coincide with that of the standard. The lower density of waters from rivers of Eastern Transbaikal should be noted.

When comparing these two tables it can be seen that almost in all cases lake water is denser than river water. The value of the densities for lakes of different character is constant enough. Unexpected is the fact that the lake of the desert Kara-Kul in the high mountains, where the evaporation process is especially intensive, has a water density which not only is not higher, but is even lower than the densities of all other lake waters with the exception of the lake Baikal. This, however, can be explained by the fact that the lake Kara-Kul receives its water from thawing glaciers and the density of its water is the result of the action of two factors: an intensive evaporation and the feeding with thawed water.

It should also be noted (Table 3) that the density of the Baikal water (though taken from a considerable depth) is lower than that of the standard.

* The comparison of the two modifications of this method will be given in a special paper.

Table 2

Density of River Water

Name of river	Place of sampling	Date of sampling	Difference in density compared with the standard, γ
Moscow water-supply	Moscow	Nov. 4, 1939	0
Volga	Opposite the town of Kosmodemiansk (village Korotki)	July 31, 1936	0
Dnieper	In the vicinity of Kiev, near the village Starosselye, at the vivarium of the Acad. Sci. SSR of Ukraine	Sept. 11, 1936	0
Ob	Near the mouth of the river Tom, the village Braguino	Oct. 6, 1936	0
Argun	In the Transbaikal, the village Olochi, near the Nertchinsk plant	July 27, 1937	—2.4
Gasimur	In the Transbaikal, near the hamlet Trubachevo of the Gasimurosavodsky district	July 1, 1937	—2.7
Shilka	Transbaikal, town Sretiensk	Aug., 1935	—2.2

Table 3

Density of Lake Water

Name of lake	Place of sampling	Date of sampling	Difference in density compared with the standard, γ	Notes
Senege	Near the Podsolnechnaya, October railway	July 23, 1938	+2.2	
Pleshcheyevo	City of Pereyaslavl	Nov. 1, 1938	+1.8	
Razval	City of Sol-Iletzk	1937	+1.9	From the depth of 15.5 m
Kara-Kul	High Pamirs	July 16, 1937	+1.7	
Imandra	Kola peninsula, Verkny Bereg, to the north from the station Imandra	Oct., 1936	+2.1	
Baikal	Near the cap Ukhan	1935	0	From the depth of 1 200 m

As is well known, the thawing and the freezing of water lead to a fractional separation of the isotopes of water. Bruni and Strada ([6]) have shown that a reiterated freezing can be used as a method for the concentration of the heavy isotopes. Eucken and Schäfer ([7]) have studied the melting diagram of the system H_2O—D_2O. They studied also the density of waters from glaciers

and found a maximum increase in density for waters from glaciers with a narrow tongue, deeply located and thawing last. The same authors found out that the concentration of the heavy isotopes takes place in the solid phase during the freezing process, and that the light isotopes pass over into the liquid phase in the process of thawing.

It is possible that such a separation of the isotopes is the reason for the lower value of the density of water from the Transbaikal rivers, connected with the area of permanently frozen grounds. In connexion with this the density of water from the ice of a bore-hole at frozen ground station of Skovorodino was measured. The following results were obtained:

Water from transparent ice, bore-hole No. 2	$-0.8\ \gamma$
Water from turbid ice, bore-hole No. 2	$-1.3\ \gamma$

In this case we have obtained a low value even for the density of ice water, the density of the river water being still lower. Therefore the possibility of these two waters being related to each other is not excluded.

All these figures prove that the isotopic composition of river (and lake) waters is very far from being always the same. One can make the conclusion that the lakes and the rivers connected with glaciers and with the snow of high regions and, probably, with the region of permanently frozen grounds as well, have a lower density, and therefore they cannot be used as standard in the measurements of relative densities.

The possibility of having a general standard is connected with the problem as to what degree deuterium and heavy oxygen participate in the fluctuations of the summary density and whether the content of one of them in river waters is more or less constant. Only in the latter case it is possible to speak of the preparation of a general standard through the elimination of one of the heavy isotopes from water. Otherwise one would be forced to accept a conventional standard and to compare with it in the future the river waters or waters from water-supplies of those places where measurements are being made.

The comparison of the densities of certain waters from rivers and lakes of the USSR has demonstrated that:

1. As a rule lake water is denser than river water by 2γ on the average.
2. The water from rivers of Transbaikal region is lighter than that of the other rivers of the USSR that have been measured.
3. The water of rivers and lakes fed with the melting ice and snow has a lower density and cannot be used as a standard for the measurement of densities.

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GÉOCHIMIE

LA DISSOCIATION DES MOLÉCULES DANS LE MAGMA EN TANT QUE FACTEUR DE SA DIFFÉRENTIATION

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Nous ne possédons que très peu de données sur l'état des molécules dans le magma. Certaines conclusions logiques nous aident pourtant à éclaircir cette question. Il est bien connu que lorsque la température monte, les composés chimiques complexes tendent à se dissocier en composés plus simples. Il n'y a que les oxydes et les éléments libres qui peuvent subexister aux très hautes températures. Il est donc raisonnable de supposer que le même phénomène a lieu dans le magma: à mesure que s'élève la température de la masse en fusion, il se produit une dissociation des molécules minérales complexes en molécules plus simples. D'autre part, il n'est pas possible d'admettre que cette dissociation s'opère au moment où le minéral cristallisé passe à l'état de fusion, autrement dit que toutes les molécules dans le magma soient dissociées. S'il en était ainsi, le processus de cristallisation et de différentiation du magma conduirait toujours à des solutions résiduelles fortement alcalines, ce qui en réalité ne se laisse constater que dans des cas relativement rares. Cette dernière circonstance atteste qu'au moment de la cristallisation du plagioclase basique, de l'augite et des hornblendes, les molécules d'albite et d'orthose dans la masse en fusion se trouvent déjà à l'état associé. Les relations observées entre quelques autres minéraux confirment la vraisemblance de ce tableau.

Nous pouvons admettre que dans le cas général la température de fusion et la température de dissociation du minéral ne coïncident pas. Les minéraux peuvent être répartis en trois groupes d'après le rapport de ces températures.

1. La température de dissociation est supérieure à la température de fusion. Le minéral fond d'une manière congruente.

2. La température initiale de dissociation est inférieure à la température de fusion. Les différents minéraux ou associations de minéraux formées lors de la dissociation fondent à la température de dissociation. Le minéral fond d'une manière incongruente.

3. La température initiale de dissociation est inférieure à la température de fusion. Tous les minéraux et leurs associations formées au cours de la dissociation fondent au-dessus de la température de dissociation. Le minéral se dissocie à l'état solide et ne cristallise pas dans la masse en fusion (grossulaire).

Si les températures de fusion et de dissociation coïncident pour certains minéraux, elles peuvent devenir différentes au cas où les conditions thermo-

dynamiques changent (par exemple, la pression). C'est pourquoi ces minéraux ne méritent guère d'etre rangés en un groupe autonome. Il est logique de présumer que pour les minéraux qui fondent d'une manière congruente, l'intervalle de température entre la fusion et le début de la dissociation peut être très variable: lorsque la température s'élève, certains minéraux se dissocient peu après la fusion, d'autres restent longtemps encore à l'état non-dissocié dans la masse fondue.

La formule générale des minéraux magmatiques anhydres peut etre représentée comme suit: $mA.nB.p\mathrm{SiO_2}$, où A sont les oxydes correspondant aux ions à potentiel bas (Na_2O, K_2O, CaO, etc.), B—les oxydes répondant aux ions à potentiel moyen (MgO, FeO, Fe_2O_2, Al_2O_3, TiO_2, etc.) et m, n et p—des coefficients numériques entiers ordinairement petits. Pour les valeurs de m, n, et p égales à zéro, nous passons de cette formule générale (type des feldspaths) à des formules plus simples (types de la wollastonite, de l'hypersthène, de la pérowskite, du corindon, du quartz). En cas d'excès d'oxydes B, ils se combinent entre eux, donnant des minéraux du type de l'almandin ($n_1B_1.\ n_2B_2.p\mathrm{SiO_2}$) et du type du spinelle ($n_1B_1 \cdot n_2B_2$). Le sous-groupe B_1 répond à des oxydes plus basiques, le sous-groupe B_2 à des oxydes plus acides.

La simplification des molécules au cours de leur dissociation dans le magma peut être réduite à deux types principaux:

1. Perte d'une certaine quantité de silice, la formule chimique du minéral restant du même type (hypersthène—olivine, orthose—leucite) ou se simplifiant (sillimanite—corindon).

2. Dissociation des molécules du type des feldspaths en composés plus simples (dissociation de l'aegirine).

Les oxydes A et la silice étant plus actifs que les oxydes B, ces derniers sont libérés lors de la dissociation avec formation, à partir des molécules du type des feldspaths, de molécules du type de la wollastonite. C'est précisément ainsi que se fait la dissociation de l'aegirine; de même dans la dissociation du grossulaire, il y a mise en liberté d'une molécule de wollastonite. La cristallisation aux hautes températures du spinelle dans les magmas répondant à un mélange d'anorthose et d'olivine montre également qu'à ces températures la molécule d'anorthose est dissociée en wollastonite et alumine libre. Les oxydes B libérés lors de la dissociation des molécules du type des feldspaths se combinent volontiers entre eux en molécules du type du spinelle fort stables aux hautes températures.

La dissociation des molécules dans la masse en fusion influence la différentiation du magma et ses produits de deux manières différentes:

1. Certains constituants des molécules facilement dissociables peuvent être éliminés du magma aux stades initiaux de la cristallisation avec enrichissement de la masse fondue en constituants restants. La fusion incongruente et les relations réactionnelles connexes des minéraux se rapportent ici comme un cas particulier (cristallisation de l'olivine à la place de l'hypersthène et de la leucite à la place de l'orthose avec enrichissement du magma en silice). La molécule de néphéline paraît se dissocier assez facilement dans le magma, et aux premiers stades de la cristallisation l'alumine peut entrer dans la composition du plagioclase, de l'augite ou de la hornblende. Le magma résiduel s'enrichit en Na_2SiO_3, ce qui peut conduire à la formation, aux stades ultimes de la cristallisation, d'aegirine, voire de niobo- et de zirconosilicates de sodium.

Tous les magmas basaltoïdes, les alcalins y compris, sauf quelques types très rares, renferment suffisamment d'alumine pour saturer complètement le sodium et même partiellement le calcium. La formation de l'aegirine est donc due à une élimination excessive de l'alumine au cours de la différentia-

tion. Dans les trachydolérites on peut constater assez souvent l'association du plagioclase basique des phénocristaux avec l'aegirine dans la masse essentielle, alors que dans les conditions de l'équilibre parfait ils sont imcompatibles. Cela ne peut s expliquer que par le fait qu'au moment de la cristallisation du plagioclase, la néphéline se trouvait à l'état dissocié. L'aegirine se formant très facilement lors de la différentiation des magmas alcalins basaltoïdes et ne se formant qu'avec difficulté lors de la différentiation des magmas alcalinoterreux, on en peut conclure que la molécule de néphéline se dissocie dans le magma beaucoup plus aisément que celle de l'albite.

2. Dans les foyers magmatiques profonds, où le magma se trouve à une température tres élévée avant le début de sa cristallisation, il se produit incontestablement une dissociation de molécules. Lors du refroidissement des parties marginales du foyer, il y peut commencer une association de certaines molécules. L'homogénéité du magma est par là même troublée, et il doit s'opérer, analogiquement à ce qui a lieu selon le principe de Soret, une diffusion des molécules associées vers l'intérieur du foyer et des parties dissociées de ces molécules vers sa périphérie. Si la vitesse de diffusion de tous ses composants était égale, le résultat final du processus serait égal à zéro. La vitesse de diffusion étant diverse, l'uniformité chimique du magma peut être dérangée. Il est naturel de s'attendre à ce que les constituants les plus mobiles et les plus aisément fusibles des molécules dissociées possèdent la plus grande vitesse de diffusion. La partie périphérique du foyer magmatique doit être enrichie justement en ces constituants, tandis que sa partie centrale sera enrichie en constituants restants des molécules dissociées. Etant donné que les oxydes *B* ont tendance à donner des composés plus difficilement fusibles et sont en général moins mobiles, alors que les oxydes *A* engendrent des composés plus fusibles et sont plus mobiles, il doit y avoir concentration d'oxydes *A* près de la périphérie, c'est-à-dire formation d'un magma plus riche en alcalis.

Plusiuers conditions sont nécessaires pour que pareil phénomène soit possible.

1. La vitesse de refroidissement du foyer magmatique doit être comprise dans des limites déterminées. Un refroidissement trop rapide réduira au minimum le phénomène même de la diffusion, tandis qu'un refroidissement trop lent diminuera à l'extrême l'influence des différences de vitesse de diffusion.

2. La température de dissociation du composé donné doit être comprise dans les limites de température du foyer magmatique en voie de refroidissement.

3. La vitesse de diffusion des divers constituants des molécules dissociées doit être suffisamment différente.

Ces conditions paraissent être bien observées dans quelques foyers profonds du magma trachybasaltique. L'association de la molécule de leucite lors du refroidissement de tels foyers dans la période antérieure à la cristallisation (la molécule d'orthose s'associe beaucoup plus tard) amène un enrichissement notable de leurs parties périphériques en K_2SiO_3 avec formation ici d'une envelope de magma de basalte leucitique. L'ordre de succession des intrusions dans ces gisements de roches leucitiques et les particularités chimiques de ces dernières laissent s'expliquer d'une manière tout-à-fait satisfaisante par une supposition de ce genre.

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BIOCHEMISTRY

TRANSLOCATION OF MOISTURE IN THE BULK OF STORED GRAIN

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The necessity of imposing a strict maximum limit upon the allowable content of moisture in the collected or stored grain is not to be overlooked by a grain dealer. He would be in error however to think that such a limit might be invariable whatever the other conditions of storage.

Three factors account for the separation of water from grain colloids: 1) adsorption energy between the colloids and the water, 2) amount of water available, 3) temperature both of the grain and medium. No stable boundary can therefore be drawn between the free and the bound water, and the above maximum of grain moisture is liable to change with the temperature of the repository. The rise in temperature should, other conditions being equal, change the ratio of the free to the bound water in favour of the former. The loss of weight due to evaporation processes will be the immediate result as well as awakening of ferments and microorganisms, which as soon as free water appears are likely to develop their injurious activity.

As in any air-dry system so in grain the water it includes may be credited to have a high mobility. The ratio of the free to the bound water should be expected to vary continually with temperature against the background of absolute constancy in the physical and chemical condition of the colloids.

Increased humidity will occur in places of lower temperature and conversely. The reason is that with increased temperature the vapour pressure becomes higher and the water, now more loosely held, is forced towards grain-portions with lower pressure and temperature, where it is either combined or condensed into drops.

To verify this theoretical interpretation by experiment and to draw some conclusions with reference to large-scale storing of grain was the aim of the present work which was all conducted in the laboratory.

Local cooling was artificially created in the bulk of stored grain with the intention to set-up an uneven distribution of moisture which should eventually result not only in the transfer of water but also in the formation of centres of deteriorated grain liable to spontaneous heating. By changing the moisture content in the grain under test we intended to ascertain how the degree of moisture co-operates with the difference in temperature in affecting the energy of the water transfer from one part of the bulk grain to another. A certain correlation was expected to exist between these two factors.

The experiment was run with a spring soft variety of wheat. The requisite degree of moisture was attained by immersing the seed on a sieve into water for a definite interval and by taking it up for drying on a thick cushion

of gauze. The grain for the experiment was subjected to after-drying in thermostats at 28—30° C, in layers 4—5 cm thick. The experiment itself was conducted in 6-litre glass beakers insulated with felt and oilcloth and provided with wooden lids. A little refrigerator was designed to pass through the lid and cool the grain locally. The lid was also pricked through by a thermometer. The cooled portion of grain was isolated in a gauze bag impregnated with paraffin. The bag was filled with about 60 g of the same grain that the whole vessel contained. The refrigerator was a short cylindrical glass vessel of about 20—25 cm^3 capacity. It had one inlet and one outlet tube sealed in and insulated from the rest of the grain by a double glass muff closed hermetically.

The results of the test are summarized in the two following tables. The first presents data obtained at room temperature, while the figures of the second refer to a higher temperature adjusted by means of a thermostat.

The conclusion which follows from the tabulated data is that grain gives off water to its cooled portions. Small difference in temperature suffices for the water to be delivered in that way as is shown by experiments 4 and 5, where it was only 1—3° C during a certain time. We should indeed be surprised by the striking responsiveness of the grain. It is very likely that the most perfect conditions of storage and especially transportation of grain cannot prevent this travelling of the moisture.

The translocation of moisture due to the difference in temperature was stated in that case too when the water content of the grain was very low, and we did not yet come to the limit while reducing it lower and lower.

Most representative in that respect are the experiments 1 and 11 with a grain low in moisture. Here moderate temperature and reasonable cooling of a portion of grain were attended by the travelling to this portion of distinctly observable and readily measurable amounts of water.

The latter effect was observed in the experiment 13 which started with only driving the water without any detriment to the cooled portion of grain, but ended in creating conditions for the corruption of grain soon after a greater difference in temperature had been adjusted by somewhat stronger cooling.

This was the first proof of the possibility for the grain to be spoiled while in a condition of a very low moisture, which is usually classified as perfectly dry (9.8% of moisture).

The only factor in corruption was the disturbance of the temperature uniformity which led to the translocation of water from one part of the stored grain to another. The fact that in a grain with such a low content of moisture considerable amounts of water can travel and spoil it, requires careful consideration in both theoretical and practical aspects.

With all that we can no longer be astonished by having observed a similar corruption in the grain higher in moisture (13.1—14.6%). It is not difficult to understand why here a lesser difference in temperature was sufficient to bring about the same results. The spoiled portion of grain in the experiment 15 has been photographed, and in Figs. 1 and 2 we can see clearly that a number of grains have germinated into long etiolated sprouts.

If the content of moisture is raised above the standard to a value ranging between 16 and 20.5% (experiments 7, 8, 9, 10, 16, 17), a much lower difference in temperature will suffice for creating the centres of corruption.

The length of the interval between the inspections, during which air was kept away from the grain, was found to play an important rôle in corruption. On inspection the grain was poured out of the vessel and the bag with the tested aliquot was opened. This accounts for the much more effective results of the experiment 7, compared to 8, 9 and 10, since this was run without interruption, and the grain was not inspected until the end of the experiment.

Table 1

Experiments with the Bulk of Grain Kept at 16—17°C

No.	Grain moisture in % of damp material			Degree of cooling in °C	Duration of experiment	Condition of grain in the cooled portion
	Initial of the whole grain	Ultimate of cooled portion	Ultimate of the bulk of grain			
1	9.1	10.3	9.0	8	30	Without change
2	13.9	14.8	—	5	33	» »
3	14.7	18.0; 22.3	—	7	66	» »
4	15.1	15.4	—	1.2	31	» »
	15.1	16.8	—	4.5	+ 39	» »
5	15.1	16.3	—	3	31	» »
	15.1	18.2	—	6	+ 42	» »
6	15.3	16.5	—	7	50	» »
7	18.8	30.4; 68.3	17.9	7	29	Germination, mold
8	20.1	25.0	19.5	7	13	Mold
	20.1	22.6	—	5	+ 30	Mold
9	20.5	23.1	—	6.5	14	Mold
	20.5	22.8	—	5	+ 13	Mold
10	20.4	24.5	—	8	26	Mold
	20.4	20	—	6	+ 53	Mold

grain frequently aired while inspected

Table 2

Experiment with the Bulk of Grain Kept at 23.5, 26* and 28°C**

No.	Grain moisture in % of damp material			Degree of cooling in °C	Duration of experiment	Condition of grain in the cooled portion
	Initial of the whole grain	Ultimate of cooled portion	Ultimate of the bulk of grain			
11	8·2	8.9	8.2	13	33	Without change
12	9·5	11.7	9.5	15·5	22	» »
13*	9·8	13.6	—	12	73	» »
» *	»	16.4;36.2	—	20	+14	Germination, mold
14	13.1	16.7;42.8	12.3	16	18	» »
»	»	18·8	—	16	+ 7	» »
»	»	29.0;64.7	—	16	+18	» »
15*	14·6	22·9	13.8	14	33	Germination, mold (photograph)
16	16.0	18.5	16.2	10; 0 (50 days without being cooled)**	81	Mold partly affecting the rest of the grain
17	19·1	28.1;35.9	—	16	11	Germination, mold, bacteria, slime
»	»	79.1	13.2	16	+39	Long sprouts, bacteria and molds fused into a slimy mass
»	»	15.2	—	0	+28	Dried fused mass

Naturally enough, the moisture was distributed in the tested aliquot not uniformly, but its different gradients were lying along the radii to the centre occupied by the refrigerator. A very representative example of such a distribution of moisture in the aliquot was furnished by the experiment 3 where the external response of the grain to the change in its water content was only by increasing the volume.

It is only when the difference in temperature between two portions of bulk grain disturbs the available equilibrium in the distribution of moisture and sets up a new one that it becomes quantitatively apparent as a factor creating a higher moisture in the portion of lower temperature. This is evident from the data of the experiment 4 where as low an increase in the difference between the temperatures as some few degrees was high enough to raise the moisture of the cooled portion by 1.4% at the expense of the rest of the grain. This phenomenon recurred in the experiment 5. An opposite effect was produced by decreasing the difference in temperature in the experiments 8, 9 and 10 where the uneven distribution of moisture was not only essentially smoothed (exp. 8 and 9), but even perfectly levelled (exp. 10) as the difference in tempe-

Fig. 1. General aspect of the bag with cooled grain taken out of bulk; grain sprouts appeared outside. A lump of fused moldy grains stuck below.

Fig. 2. The inside of the bag with refrigerator placed in it. Half-fused mass of partly germinated grains.

rature vanished. It is well here to refer once more to the experiment 13 in which strong local cooling greatly enhanced the temperature difference and the grain at the place of cooling was spoiled entirely as early as in two weeks, though its condition during 2.5 months preceding the experiment had been quite normal. The reverse was the case in the experiment 17. Here the focus of increased moisture and corruption created by cooling was destroyed by levelling the temperature, and only a dry fused lump of completely spoiled grain remained amidst the bulk of whole grain.

If the difference in temperature between the aliquot grain and its surrounding bulk grain was kept constant, as in experiment 14, the moisture was observed continually to accumulate in the former, and the limit to which such a system should naturally tend was not reached, because germination, which seems to be due to the deposition of water drops (see below), set in.

The foci of increased moisture created by uneven distribution of temperature in the bulk of stored corn can spread the corruption in the form of molds, from which they are first to suffer, to the neighbouring grain and farther around. Experiment 16 was started with creating a focus of lower temperature by cooling the aliquot to 10—12°. Then the grain was allowed to rest at about 27—28° C. The result was that the grain in places of cooling was strongly affected with mold and more moist than the rest of the grain, which,

however, was also pervaded with certain amounts of mold from the centre of cooling.

The reason which may be put forward to account for the germination of grain, observed in some of the experiments, is that the moisture collected from the air on the surface of the cooled grain and refrigerator in the form of drops was conveyed by capillaries to the grain not in the immediate neighbourhood of the refrigerator. Such a capillary transmission of water from the place of cooling is no less probable than a gradual deposition of dew on the very grain, which should quickly suck in water while it is being deposited. Furthermore the capillary transmission of water through the interstices between the grains is supported by the lack of uniformity in the distribution of the grains which have germinated among those which have not and show varying degrees of swelling, as it was stated on estimating the moisture in the separate groups of the aliquot grain (experiments 13, 14 and 17).

The effect of the water which either as vapour or condensed into drops travels from the more to the less warm grain increasing the water content of the latter is strengthened by the respiration process in the sufficiently damp grain, which goes to increase the accumulation of water and is therefore also an important factor in creating the centres where a spontaneous heating of grain is apt to arise. The significance of those added amounts of water is obvious from the fact that the grain was observed also to decrease in dry weight. Though this loss was only 4—5% in some cases, it amounted to 22% in the experiment 17, i. e., the ratio of respired water was 8.8%, if calculated with respect to the dry weight of the grain.

The data obtained have undeniable practical bearing upon grain storage, since they point to the fact that the bulk of grain of a very high standard with regard to the moisture content is not safe from the danger of being spoiled, unless due care has been taken to provide for most uniform temperature throughout its volume.

When the grain is to be emptied in a repository, the difference in temperature between its different portions must conform to its content of moisture. If it is higher than it should be under the given conditions of moisture, the more cool portions will invariably attract water from the other parts and the dangerous centres of spontaneous heating and ignition will eventually arise.

The standard thus established cannot be universally applied under any other conditions of grain storage, since it fails to consider the absolute value of temperature in the grain. The higher the temperature, the lower is its allowable difference between various portions of bulk grain.

The object of our further investigation—which is now to be done in a systematical way along the lines traced by the preliminary experiments here reported—is to explore the relations between the temperature difference and the content of moisture for making it possible to set definite standards of a legitimate range of temperature for the grain stored in the bins of an elevator according to varying degrees of its moisture.

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BIOCHEMISTRY

SOME DATA ON INHERITANCE OF CHEMICAL COMPOSITION BY HYBRIDS BETWEEN *N. TABACUM* and *N. GLAUCA*

By V. D. TIKHVINSKAJA

(Communicated by A. N. Bach, Member of the Academy, 2. VII. 1939)

The question as to the inheritance of chemical composition in the case of plants' hybridization is of great theoretical and practical interest. Relative to various species of *Nicotiana* a series of works by Soviet investigators appeared within recent years[1–3]. At the Institute for Botany, Ukrainian Academy of Sciences, this problem was approached in connexion with some previous works on the genesis of the alkaloids in tobacco and their physiological rôle in the plant[4–7].

Development of the experimental plants. *1*—*N. tabacum* Dubeque 44/39; *2*—*N. glauca*; *3*—hybrid F_1 *N. tab.* Dubeque×*N. glauca* (22. VII. 1938).

In the year 1938 an experiment of a preliminary nature was arranged by the present author with the aim to ascertain the character of nicotine inheritance in crossing certain species of *Nicotiana*. The experiment was carried on at the Department of Chemical Plant Physiology of this Institute under the direction of Prof. Kusmenko.

The seeds of *N. tabacum* Dubeque 44/39 and *N. glauca* as well as of the hybrid F_1 obtained by crossing these two initial forms were planted in the spring of 1938. The seed material for the test was received from M. F. Ternovsky (Krasnodar). The plants were grown from the stage of seedlings under conditions of a vegetative experiment in soil cultures. The fertilizers NKP in a proportion of 2 : 2 : 1 were introduced with the soil in the vessels of 10 kg air-dry soil capacity. In addition, on June 30 each of the plants received 2.3 g of NH_4NO_3 dissolved in the water supplied to the plants from below. In growing the plants a constant soil humidity was secured in the vessels, equal to 60% of total moisture capacity.

Ordinary phenological observations were made on the plants throughout the vegetation period. The length of the latter from germination till the outset of flowering was, under conditions of our experiment, 78, 120 and 85 days for *N. tabacum* Dubeque 44/39, *N. glauca* and their F_1 hybrid, respecti-

vely. The hybrid plants showed a certain heterosis in growth, as it may be seen from the adjoined photograph in which the Fig. *1*, *2* and *3* refer to the tested varieties in the order indicated above.

By their colour and leaf area the hybrid plants approached to the first parent, *N. tabacum* Dubeque 44/39. The respective leaf area of the plants subjected to chemical analysis is given in Table 1.

Table 1

Leaf Area in cm²

Sample	Leaf node			Total area of 3 leaves
	12	13	14	
N. tabacum Dubeque	458.7	519.7	531.6	1510.0
	412.5	498.9	502.8	1414.2
N. glauca	246.4	312.7	294.8	853.9
	242.5	284.1	311.2	837.8
Hybrid F_1 *N. tabacum*×*N. glauca*	583.0	498.9	426.2	1508.1
	461.4	519.7	559.2	1540.3

The dynamic of some chemical substances in the leaves of experimental plants was studied by taking samples 3 times during the vegetation period. The first leaf samples were taken when the first flower had appeared on the plants; the second and the third 10 and 20 days later, respectively. The leaves for the chemical analysis were always cut from the same node and at a constant hour of the day. Three leaves from the 12th, 13th and 14th nodes made one sample. They were fixed in a dry chamber at 100°C for 15 min. Drying was completed at low temperature and the leaves were ground in a porcelain mortar. The leaf area was measured by the planimeter Amsler-Koradi, the outlines of leaves being preliminarily delineated. Previous to fixation the leaves were weighed and samples for the determination of absolutely dry weight were taken immediately. In the leaf samples thus prepared the following quantitative estimations were made: of the total nitrogen according to Kjeldahl, protein nitrogen according to Barnstein, nicotine after the method of Bertrand-Javillier modified by Chapin, and the total of alkaloids by the method of Keller modified by Bodenard. The results expressed in mg per unit leaf area are represented in Table 2.

Table 2

Content of Total Nitrogen, Protein Nitrogen and Alkaloids in the Leaves of Tobacco in mg per 1000 cm² of Leaf Area

Time of sampling	*N. tabacum* Dubeque 44/39				*N. glauca*				Hybrid F_1 *N. tab.* Dubeque×*N. glauca*			
	Total N	Protein N	Nicotine	Total of alkaloids	Total N	Protein N	Nicotine	Total of alkaloids	Total N	Protein N	Nicotine	Total of alkaloids
Flowering	81.3	50.3	47.7	114.9	117.4	102.0	9.7	44.3	70.6	60.3	5.0	47.1
1st decade	69.9	57.2	54.2	93.0	84.2	75.8	7.6	44.1	66.2	58.4	3.1	52.2
2nd decade	46.4	37.9	67.6	98.8	80.3	77.2	1.6	181.5	54.7	51.7	0.7	93.4

The data of chemical analysis have shown the hybrid plants to approach the parent plant *N. tabacum* Dubeque as to the content of total and protein nitrogen. In all of the 3 groups tested the leaves decrease in total and protein nitrogen as the plants grow. As to the alkaloids, they are transmitted by heredity to the hybrids from the second parent *N. glauca*. From the data of Table 2 it is obvious also that the leaves of *N. tabacum* Dubeque increase in nicotine gradually. At the same time it may be seen that the leaves of hybrid plants as well as those of *N. glauca* decrease in the alkaloid precipitated by silicotungstic acid until its content is only tenths and even hundredths per cent. But the total of alkaloids goes up rather quickly both in the hybrid F_1 and in *N. glauca*. Toward the end of the second decade after flowering the amount of alkaloids in the leaves of the hybrid plants is twice its former value. This must be taken to mean that the alkaloid of *N. glauca*, anabasine, is hereditarily transmitted to F_1 hybrids when this species is crossed with *N. tabacum* 44/39 Dubeque. Unfortunately, it was not possible to estimate the anabasine itself in the material used in the experiment. The work has been continued this year. A more detailed investigation of the alkaloid complex in the F_1 hybrids from *N. tabacum* Dubeque × *N. glauca* is planned with the use of improved analytical methods.

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GENETICS

CHROMOSOME COMPLEMENT IN BUFFALO (*B. BUBALIS* L.)

By G. M. PKHAKADZE

(Communicated by N. I. Vavilov, Member of the Academy, 11. VII. 1939)

Repeated attempts to hybridize the buffalo with ordinary cattle are known to have been made for obtaining new animal breeds uniting the characters of both species. All these attempts, however, proved futile.

In solving the question as to the causes of the incrossability of these species, interest belongs to the difference, versus similarity, of the caryotypes of cattle and of buffalo. The success of a cross between two forms, it is true, does

Fig. 1. *a*—metaphase of the I maturation division; *b*—spermatogonial plate; *c*—plate with tetraploid number of chromosomes.

not always depend on the similarity of chromosome shape and number; however, a clear notion of this point undoubtedly contributes to the knowledge of the causes of incompatibility of the species to be crossed and facilitates further search of means to overcome the incrossability of such forms.

With this aim in view we have investigated the caryotype of buffalo and made chromosome counts in spermatocytes, and, in part, in spermatogonia of testes taken from 2—3-year-old animals. The material was fixed after Minuchi and Painter-Allen and stained after Haidenhain (iron haematoxylin), after Newton and partly after Feulgen-Rossenbeck. Sections were 12 microns thick. Drawings of the equatorial plates were made with eye-pieces × 10 and × 20, immersion objective lens 1/12; the tubus was drawn to 170 mm. The drawings were made with the aid of Abbe's camera lucida.

For chromosome counts were used almost exclusively equatorial plates of the I maturation division. As to the spermatogonial plates, they proved to be unsuited for chromosome counts, owing to their crowded condition.

Chromosomes of the I maturation division (Fig. 1) in the majority of cases are arranged within the plate in a definite order. The larger chromosomes are, as a rule, located peripherally, whereas the smaller ones assume central

position. However, in some of the cells a somewhat different spatial relation between the small and large elements is observed.

The number of larger chromosomes located at the periphery is equal to 12. It should be noted that nearly each of the eight small chromosomes exhibits a transversal cleft which, we are convinced, is due to reductional splitting. As to the larger chromosomes, no such clefts could be found in them safe for a few exceptions. These clefts in the small chromosomes are sometimes so conspicuous that they make it difficult to decide whether we are dealing here with two different bivalent chromosomes, or with partners of a single bivalent chromosome. This circumstance renders exact chromosome counts very difficult (Fig. 1, *a*, *b*, *c*).

A study of a sufficiently great number of metaphases of the I maturation division made it possible to establish the presence of 28 bivalents (Fig. 1, *a*). In those spermatogonial plates where the number of elements could be counted, we have found the diploid chromosome number to be equal to 56 (Fig. 1, *b*).

The chromosomes in spermatogonia show usually a mace-like shape. More seldom they have the appearance of long and thin or short and thick rods. Besides, there are several V-shaped and several oval chromosomes. The number of the most typical V-shaped chromosomes is equal to 4—6, i. e. considerably exceeds that in bull, in whose spermatogonial plates Krallinger(1) has found only one V-shaped element.

The buffalo, thus, differs from the bull not only in its chromosome number being equal to 60, but also in the chromosome morphology.

In one of the slides we have found an equatorial plate of the I maturation division which exhibited a tetraploid chromosome number, 56 (Fig. 1, *c*). The discovery of a tetraploid plate is of interest in respect to the doubling of the chromosome number in the sex cells in buffalo and to the frequency of this phenomenon.

One may, thus, conclude from our observations that one of the reasons responsible for incrossability of buffalo with cattle is the difference in the chromosome number of these species which amounts to four in a diploid complement. The same is true of the yack which was found to possess 60 diploid chromosomes.

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PLANT ANATOMY

DEVELOPMENT OF ENDOSPERM IN CEREAL KERNEL AND ITS MORPHOLOGY

By V. G. ALEXANDROV and O. G. ALEXANDROVA

(Communicated by A. A. Richter, Member of the Academy, 28. VI. 1939)

In 1898 Navashin while reporting the phenomenon of double fertilization interpreted the endosperm of *Angiospermae* on the basis of its development history as a second, though non-differentiated embryo. This statement was supported later by a number of other investigators and is now generally considered a well established fact.

The authors of the present paper after having studied numerous instances of endosperm development in various wheat forms incline to the opinion that many new links may be added to the chain of logical conclusions put forward by S. G. Navashin as to the embryonic nature of the endosperm. Their argumentation is as follows.

When the structure of the endosperm in a wheat kernel is examined on cross-sections, a sharp difference in size may be seen between the cells of the aleuronic layer and their adjoining cells of the so-called starchy portion of the endosperm. Especially striking is this difference on the lateral sides of the kernel [Fig. 1, part of a cross-section of a wheat kernel in the stage of «waxy» ripeness; Tulun 7A/44 (v. *milturum*) from Khibiny]. So great a size difference between two contiguous cell layers is sometimes evidence for the different origin of the respective histological elements. The presence of plasmodesms between the cells of both layers disclosed by Günther(1) is by no means a disproof of the supposition as to the different histogeny of the layers, since the plasmodesms can possibly be of secondary origin.

The initial differentiation of the endosperm in cereals is the first to follow after fertilization. It is not until a sufficient number of nuclei have formed in the endosperm that the first partition arises in the fertilized egg cell(2).

Fig. 2, a part of longitudinal section, presents a wheat seed, variety Moskovskaja 2411, having started development soon after fertilization. The basal end of the endosperm is already a strong formation, while the embryo, near the decaying synergid, is still passing the first stages of differentiation.

Special attention seems to be due to the fact that the endosperm when starting development is in contact with the antipodal apparatus. Among the cereals from the tribe *Hordeae* the location of large, strongly vacuolated antipods in an embryosac ready to fertilization is in the placental chalazal region of the cotyledon. A special converging system extends to this region which afterward becomes the kernel's furrow. The antipods are attached to the placental chalazal region until their disappearance and undoubtedly are intermediary anatomical elements between the system conveying nutriment to the

cotyledon and the developing contents of the embryosac. That zone of forming cereal fruit where the placental chalazal region is located is considerably drawn out in length soon after fertilization, and with it the young kernel grows lengthwise, too. Naturally enough, the cells of the antipodal apparatus move thereby asunder and this rather dense tissue becomes very loose.

An interesting point to note here is that in cereals the cells of polar nuclei are from the very start of embryosac differentiation attached to the antipodal

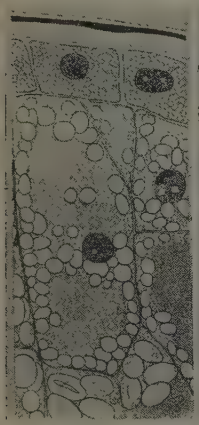

Fig. 1.

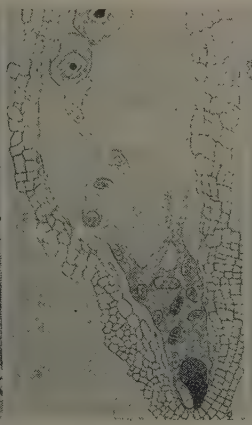

Fig. 2.

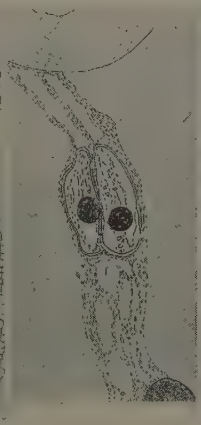

Fig. 3.

Fig. 4.

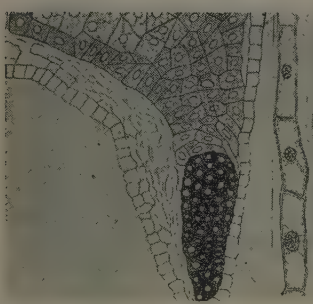

Fig. 5.

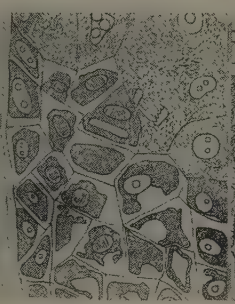

Fig. 6.

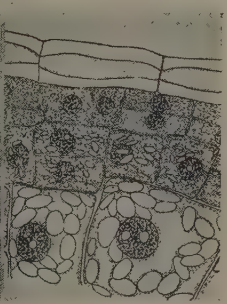

Fig. 7.

apparatus at the one end and to the egg apparatus, at the other. This position of the cells of the polar nuclei was reported by Cannon[3] in the embryosac of wild oat as early as in 1899. Fig. 3 presents the polar cells with their nuclei from an embryosac of wheat variety *Lutescens* 062, gathered at the pasture Abago (Caucasus National Park; altitude 1800 m). What is shown in the figure are only parts of a huge antipodal and an egg cell (densely shaded with dots) with the cells of the polar nuclei drawn out between them. The protoplasm of the cells is strongly vacuolized, the eggs are covered with a distinct and a rather thick membrane; within each of the nuclei is a large round nucleolus. The nuclei are in close contact with one another. The intimate union of the polar nuclei cells with the antipodal and egg apparatus is by no means a matter of chance. But though much may be supposed about these relations, nothing is definitely khown as yet.

While the cereal embryo long remains in the condition of a blastomere (the result of the first division of a fertilized egg cell), the endosperm exhibits strong growth and rapid differentiation. The basal part of the endosperm immediately adjoining the embryo consists of a compact solid syncytium with dense granular protoplasm and large nuclei; no cellular walls are present during the first phase of its formation. The upper portions of the young endosperm are lining the cavity of what formerly was the embryosac, covering the walls of the latter with thin layers of granular protoplasmic mass containing nuclei which are as well expressed here as in the dense syncytium. Fig. 4 presents a longitudinal sagittal section of a young kernel, hard wheat variety *Hordeiforme* 027, with its endosperm starting formation. The first stages in the formation of a cereal endosperm following fertilization do not appear to have been investigated; at least we failed in our attempts to find such information in literature. And Guignard([4]) has even emphasized the difficulty of such a study because of the very rapid division of fertilized polar nuclei. Special efforts are to be made along this line. The whole body of the young endosperm represented in Fig. 4 strongly suggests the blastula of an embryo starting development in certain animals([5]). The similarity between the blastula of a cereal endosperm and that in the insect *Pieris crataegi* described by Bobretsky extends as far as to the type of their formation. According to Guignard, the first location of the endosperm nuclei is within the parietal protoplasm of the embryosac. This is also seen in Fig. 4. Doubtlessly, the blastula-like organization of the embryo beginning development owes its formation and growth to the presence and growth of the embryosac, and its primordia appear very early, immediately after fertilization.

Antipodals are known to be soon obliterated and leave nothing but insignificant traces.

Consequently, the first period in the development of the cereal endosperm is to differentiate up to a blastula-like organization, whereas the real embryo is only a blastomere during that time. At this first phase following fertilization the endosperm is not only well ahead of the differentiation of the true embryo, but the very trend of this process is suggestive of the initial stages in the embryogeny of animal organisms.

The first partitions between the cells arise in the basal dense part of the endosperm. The rest of the endospermal mass which has become a cavity of the former embryosac, is for a rather long time only a ropy protoplasm with numerous nuclei, passing different stages of division, dispersed in it. By and by it fills up this cavity. At length the cellular partitions are formed in this mass, too, and in the cells themselves starch grains begin to appear. This stage in the formation of the endosperm is shown in Fig. 5, which presents the lower part of a young kernel of soft (speltiform) wheat from Afghanistan. When the cell walls appear in the mass of endosperm filling up the cavity of the former embryosac, the true embryo is already a great number of cells, but still preserves the condition of a blastomere. The stage of the embryo development described here and shown in Fig. 5 may be regarded as the climax in the differentiation of the endosperm as the second embryo. It is complete when the cavity of the blastula-like formation arisen in the embryosac immediately after fertilization is filled up. The further differentiation of the endosperm is a degradation of its embryonic nature.

The question arises here, to what extent does the endosperm differentiate as the second embryo and what are the signs of its degradation?

In Fig. 5 we see a tissue consisting of one—three layers of cells with contents similar to that in the cells of the basal part of the endosperm to spread parietally upwards from the latter. The basal part of the endosperm stands out owing to the dense and distinctly granular structure of the protoplasm in

its cells. The endosperm cells arranged parietally form a kind of epithelium for the blastula-like formation (blastoderm) and are the initial cells of the aleuronic layer. As to the origin of the cells filling up the cavity of the former embryosac, they have been formed (first, by way of free formation of nuclei) within the mass of this tissue out of that portion of the basal region of the endosperm which has turned into cavity, and partly by way of division of the cells arranged parietally.

As the true embryo grows and develops, its dissolving action becomes apparent on the cells of the basal part of the endosperm which eventually disappears almost entirely, so that nothing but a thin layer of strongly obliterated and fused cells is left. This is shown in Fig. 6 where a summer wheat from Sweden (sagittal section as in all the figures except 1 and 7) is taken to exemplify the dissolved condition of cell contents in the basal portion of the endosperm. That this portion which adjoins and even envelops the young embryo is used up by the latter for development, has been shown with especial clearness by Krauss ([6]). What remains intact is the aleuronic layer and the starchy part of the endosperm both continuing their differentiation. Thus, the cells of the aleuronic layer can divide not only radially or across, that is in the direction of kernel growth, but also tangentially (Fig. 7, cross-section through the middle of a young northern early ripening kernel), whereby they come into contact with the cells of the starchy tissue, filling up the cavity of the former embryosac. However, their division in this direction is far less intense than that proceeding radially or across. Therefore, the division of initial cells of aleuronic layer yields products which in most of the cases are not deeply distributed in the endosperm tissue except the region of the furrow.

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MICROBIOLOGY

CHANGES IN THE AMOUNT OF MICROORGANISMS IN ELECTRICALLY DRIED GRAIN

By A. A. EGOROVA

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The questions connected with grain storage in view of their economic importance have been included in the working plant of the Academy of Sciences of the USSR. In that connexion we had to try the work of a drying electrical disinsector derived by Ing. Vorobiev. The test was done at a collective farm in the Dnepropetrovsk province 17 km from island Khortitza by an expedition of biologists. The task set before us (Egorova and Sokolova, chemist) was to ascertain how the microflora usually present in great amounts on the grain surface ([1],[2],[3]) is influenced by drying the grain in Vorobiev's apparatus with varying doses of infra-red rays. Since the experiment was conducted outside the laboratory, the action of the radiant energy could not possibly be separated from the action of the thermal energy and this was not necessary, indeed. Accordingly, our data show the cumulative effect of drying upon the microflora of wheat grain (Ukrainka and *Hostianum*). The grain was made to pass through the drier according to the procedure generally adopted in practice. Having passed through the drier, the grain contained a far smaller number of microorganisms that it had had when emptied into the bin. From this point of view the apparatus met its intended purpose and doubtlessly it was of interest to follow the relation between the number of microorganisms in the grain and the various processes of the treatment it underwent while passing through the drier. In other words, we had to analyze the operations of the drying device, as we had it already done with respect to the grain from the spike which successively passed the combine and the drier (Table 1).

Table 1

Number of Microorganism Colonies per 1 g Grain (in millions)

Medium	From spike	From combine	From bags
Meat-pepton-agar	20	43	304
Wort-agar	1	Many	197
Wheat-agar	2	10	292

To closely follow the run of grain purification from the microbiological point of view we took samples from: 1) the bin where the grain had been

collected—control; 2) the chamber where it had been irradiated under varying temperature conditions; 3) the refrigerator wherein it was kept after having left the chamber.

The temperature conditions in the irradiation chamber were 50, 55, 60, 75 and 80°C. They were always set for 1 min. The temperature of the radiator elements was: No. 1—859°, No. 2—879°, No. 3—674°, No. 4—590° and No. 5—289°C (as measured by Zelenina and Klimov). In the irradiation chamber the temperature never dropped below 70—110°C, whereby the upper limit (100—110°) refers to the air in the upper diffuser and the lower limit (70—80°) to the air in the lower diffuser. The temperature of the grain itself varied according to the thickness of its layer on the ribbed drums.

While taking the samples due care was exercised to prevent contamination. The microorganism colonies developed in various mediums at 30°C were counted 24 hours later (Table 2).

Table 2

Drying $t°$ in °C	Variety of wheat	Nutrient medium	Number of colonies in the grain from			Change after exposure (in %)	
			Bin (control)	Irradiation chamber	Refrigerator	Chamber compared to bin	Refrigerator compared to chamber
50	Ukrainka	MPA . . .	304	391	16	+ 28.6	—96.0
		WA	197	412	20	+ 109.1	—95.2
		WhA . . .	292	137	15	— 52.8	—89.1
55	Ukrainka	MPA . . .	42	374	12	+ 790.4	—96.8
		WhA . . .	20	420	1	+ 2 000	—99.8
56—58	*Hostianum*	MPA . . .	230	540	180	+ 134.7	—66.7
		WA	70	680	—	+ 871.4	—
		WhA . . .	170	200	40	+ 17.6	—80.0
60	*Hostianum*	MPA . . .	230	370	170	+ 60.8	—54.1
		WA	70	220	30	+ 214.2	—86.4
		WhA . . .	170	250	60	+ 47.0	—76.0
60	Ukrainka	MPA . . .	190	3 420	250	+ 1 700.0	—92.7
		WA	150	2 250	180	+ 1 400.0	—92.0
		WhA . . .	100	610	150	+ 510.0	—75.4
75	*Hostianum*	MPA . . .	230	20	—	— 92.4	—
		WhA . . .	170	50	—	— 70.8	—
80	*Hostianum*	MPA . . .	230	30	—	— 97.0	—
		WA	70	40	—	— 40.9	—
		WhA . . .	170	90	—	— 47.1	—

Note. MPA—meat-peptone-agar; WA—wort-agar; WhA—wheat-agar.

The grain having once passed through the chamber at 50, 55, 56—58 and 60°C, we found the number of colonies to have increased compared to the control taken from the bin. The increase was rather considerable, and it would seem that irradiation in the reduced humidity of the drier (from 24.7 to 22.7%)

favoured the growth of microbes. It seemed, however, hardly probable that there could be any truth in this conclusion and a more natural cause suggested itself, namely, the contamination of the grain by microorganisms from the dusty air of the room, in which the drier was operating. In fact this air was found to abound with microorganisms (Table 3).

Table 3

Air Analysis Made by Koch's Method (Petri dish, 10 cm³ in diameter)

Place of sampling	Exposure	Number of colonies in nutrient medium		
		MPA	WA	Czapek
Bin	3 min.	246	235	63
Elevator near the bin	1 »	1 500	880	1 011
Elevator near the refrigerator	1 »	255	420	169
Irradiation chamber near the tube (motor stopped)	1 »	552	240	—
Outlet tube of refrigerator	1 sec.	2 006	1 086	—

In various parts of the drier microorganisms were also found in great numbers (Table 4). This was another ground for referring the contamination of the grain in the drier at a moderate temperature to the microflora of the air. With higher temperatures (between 75—80°C) the number of microorganisms was reduced even after the first exposure. This method, however, proved unsuitable for practice, since the quality of the grain was impaired by it. But whatever the temperature in the chamber might have been, the number of microorganisms was always reduced if the grain after having passed the chamber was forced through the refrigerator. This was probably because the grain was blown through by the air in the refrigerator, and the microflora was thus removed with the dust mechanically. The estimation of microorganisms carried by the air current away from the refrigerator (Table 3) has supported our conclusion.

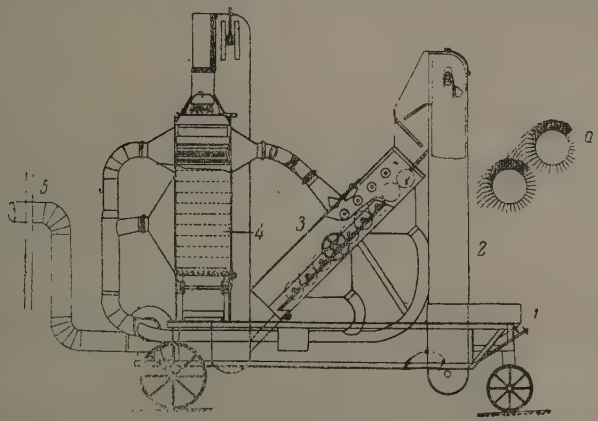
Table 4

Air Analysis

Place of sampling	Number of colonies per 5 l of nutrient medium	
	Meat-pepton-agar	Wort-agar
Bin	600 000	476 000
Upper radiators (2—3)	68 000	17 400
Lower radiators (6—7)	240 000	20 000

Only moisture was lost by the grain in the irradiation chamber (2% per minute). For the sake of further inquiry the grain which arrived from the refrigerator was conveyed through the irradiation chamber again. The results were more favourable in so far as with each new exposure the number of microorganisms dropped. The moisture of the grain went down, too. After the 4th exposure (each lasting 1 min.) it was only 17.6% as against 24.7%, its initial value. In other words, both the moisture and the number

of microorganisms decreased gradually if the grain was made to pass through the electrical drier again and again. The forms which predominated among the microorganisms were as follows: sporiferous form (*B. subtilis*, *B. megatherium*, *B. mycoides*, *B. mesentericus*, and others), non-sporiferous forms—various chromatogenous and slimy microorganisms (of the type *Bact. herbicola aureum*, *B. florescens*), yellow and pink cocci, orange and yellow sarcinas, mold fungi and actinomycetes. The sporiferous and chromatogenous forms



Drying desinsector: *1*—bin; *2*—elevator; *3*—chamber; *4*—refrigerator; *a*—ribbed drums; *6*—radiator.

proved the most resistant to the conditions of the irradiation chamber. The actinomycetes and the mold fungi showed no appreciable decrease in number.

Consequently, the grain after 4 exposures has left in the drier 7% of its moisture, and if the temperature varied between 50 and 55°C the number of microorganisms decreased after the grain was blown through many times (up to 10 times). Such a grain should be less liable to spontaneous heating when stored up in bulk. In a preliminary experiment the control grain kept in Dewar vessels was heated spontaneously up to 12° against the temperature of the ambiant air, while the grain passed 4 times through the drier increased in temperature only by 1°.

The conclusion to be drawn is that the action of the grain-drier tested is reduced to a decrease in moisture. As to the decrease in the number of microorganisms, this should be ascribed to the effect of blowing rather than irradiation. However, the cumulative effect of the apparatus devised by Vorobiev is that both the moisture and the number of microorganisms are reduced in the grain. But still better results will be obtained by modifying the construction so as to prevent the grain from contamination with the dust of the room.

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PATHOLOGICAL ANATOMY

SENILE ALTERATIONS IN THE BONY AND CARTILAGINOUS APPARATUS OF THE JOINTS

By I. L. KLIONER

(Communicated by A. I. Abrikossov, Member of the Academy, 6. VII. 1939)

Taking into account the frequency of changes (deformations) in the joints of old people, we undertook to investigate the involute processes, due to age, which take place in the joints of old people who do not suffer from joint-diseases.

For this purpose we made X-ray examinations of 106 senile invalids in the village of Yelatma, Moscow region. These people aged from 60 to 92 years were not ill. We found obvious changes in the bony cartilaginous apparatus of their joints. These changes were found to be similar in the overwhelming majority of the patients investigated, regardless of their sex and anamnesis. After we had checked our results on some old people taken at random, we became convinced that it was no disease (arthritis) we were dealing with, but the manifestations of an involute processus in joints, due to age. To establish the character and essence of this process a post mortem macroscopical and microscopical examination of the joints of 125 old people aged from 60 to 96 years was carried out at the Pathological Institute of the Sklifassovsky Hospital, under the direction of Prof. A. V. Roussakov.

The process is based on the atrophy (wearing out) of the cartilage of the joints which insues with age. Being a hyaline structure, this cartilage shows an admixture of fibrous cartilage at the places where the connective tissue of the synovial membrane of the joint capsule meets the cartilage; this is why the initial alterations set in at the edges of the cartilage

Unlike the bony tissue, the cartilage is unable to regenerate. Therefore, with age, it is subject to degeneration. The intercellular substance of the cartilage becomes lighter in colour because of the accumulation in it of liquid substances. The cartilage becomes fibrous, with a multitude of small spindle-shaped cells lying closely together and resembling fibrous connective tissue. The cartilage cells begin to dissappear. Whitish spots with empty cartilage capsules which are spots of necrosis appear. Next to them, however, begins the active reproduction of the cartilage cells which lie arranged in small heaps with a multitude of tiny atypical young cells. The uppermost layer of the cartilage wears out, its contour becomes rough and uneven. Indentations gradually appear in the cartilage. These fuse together causing large defects. This process may result in a total disappearance of the cartilage and the disclosure of the bone. The cartilage penetrates deep into the bone producing a real cartilage hernia; and the bone with its marrow penetrates into the cartilage.

This process in the cartilage is of purely degenerative character, no inflammatory or pathological phenomena whatever being involved.

At the same time regenerative processes take place in the bony tissue of the joints which assumes the work and the function of the affected cartilage. Under the destroyed cartilage there proceeds an increased internal formation of the bone. This results in sclerosis and in thickening of the subchondrial bone which consists of young growing bone tissue deficient in marrow. Intertrabecular spaces are filled with a particular fibroreticular tissue with a layer of osteoblasts lining the walls of these spaces. This tissue is often mistaken for the usual fibrous tissue that looks like it, and is erroneously interpreted as a fibrous transformation of the marrow. As a matter of fact, this tissue is the matrix of the future new bone, its presence pointing to an intensified local metabolism and increased formation of the new bone. We failed to find any signs of fibrous metaplasm of the marrow, and we deny its being involved in the senile changes of the bone. Besides the endostal growth, there is also an exostal proliferous growth of the bone, in the form of bone protrusion (osteophytes) at the edges of the epiphyses, which leads to the deformation of the joints. Osteosclerosis, as well as osteophytes, are more strongly manifested in the sockets of the joints than in the balls of the bones. In the latter bone protrusions are found mostly at the edges of the cartilage, where the capsule of the joint is attached to them, and also at the places of attachment of the ligaments and sinews of the muscles. Moreover, there can be detected in the bone itself qualitative changes of a degenerative character, namely, small cyst-like spaces filled up with chondroid and fibrous connective tissue. These «subchondroid cysts» are met with only in bones covered with cartilage. Their development seems to be connected with cartilage hernias in the bone followed by subsequent degeneration of the cartilage into connective tissue.

Thus, we have here a process of atrophic degeneration of the cartilage of the joint and a compensatory regeneration of the subchondrial bone with reactive degeneration in it. We suggest, therefore, to term this process the «senile degenerative osteoarthrosis» (more exactly, «osteochondrosis»). The cartilage is primarily affected and only after this do subsequent changes take place in the bone; if the cartilage is intact, there is no sclerosis, nor bone protrusions, nor degenerative changes in the subchondrial bone.

This process can be established during the life of the patient by the following X-ray picture: the narrowing of the joint fissure; increased sclerosis of the subchondrial compact band of the bone, uneveness and indentation of the surfaces of the bone at the joint; subchondrial cyst-like rarefaction of the bone; and chiefly, osteophytes at the edges of the bone at the joint.

These alterations set in and are more pronounced in the joints of the fingers and toes and in the small joints of the vertebral column, since these joints are overcharged functionally, the cartilage there being very thin. So-called Heberden and Boucharre knots on fingers reported for senile patients are no nosological units, but are the above-described osteophytes. The same is true of climacteric and other arthroses, as well as the much spoken-of gout, so often dragged-in to explain the diseases of old patients. Next in frequency after the fingers and toes and the joints of the vertebral column come the knee joints, where erosions of the joint cartilage with big defects of it and pronounced osteophytes of the edges on femur, tibia and patellae can be seen with the nacked eye. In the hip-joint there are great lesions of the cartilage on the ball of the femur as well as on acetabulum; edge osteophytes are found over the fossa acetabuli, where the bone tissue of faciei lunatae acetabuli overhangs and partly covers this cavity, and also on supercilium acetabuli, where labrum glenoidale is ossified. In the shoulder the osteophytes are found on the edges of cavitas glenoidalis scapulae and, to a lesser degree, at the place of attachment of the joint membrane. The remaining joints of the skeleton are affected less frequently and to a lesser degree.

The discovery of the old age osteoarthrosis calls forth a revision of the entire problem and the classification of chronic arthrosis in middle-aged people, inasmuch as in many cases arthrosis can be treated either as premature old age osteoarthrosis brought about by some harmful factors of the environment, or else as an intensification and aggravation of the senile osteoarthrosis brought about by a local lesion of a particular joint, say, by trauma, disturbance of nutrition, compulsory functional overstrain, and so on.

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PLANT PHYSIOLOGY

PHYSIOLOGICAL BASIS OF MUTUAL INFLUENCE BETWEEN STOCK AND SCION OF BEET

By A. S. OKANENKO and N. V. VANDIUK

(Communicated by N. I. Vavilov, Member of the Academy, 8. V. 1939.)

The object of our previous works ([1,2]) was to throw light upon the rôle played by the assimilation apparatus and some physiological particulars of beet roots in their ability to store up sugars. With that purpose in mind we grafted the leaves of the sugar beet upon the roots of the table beet and vice versa at an early age of the plant. Some of the data obtained in that way are referred to in Table 1.

Table 1

Sugar Content Induced by Various Graftings

Scion/stock	Weight of root in g	Sugar content in root (% of dry weight)		
		Reducing sugar	Sucrose	Total
Sugar variety / Table variety	210	0.1 / 0.1	12.4 / 8.4	12.5 / 8.5
Control (sugar variety)	540	0.25	8.25	8.50
Table variety / Sugar variety	255	0.1 / 0.1	5.6 / 11.9	5.7 / 12.0
Table variety / Sugar variety	410	—	—	10.6 / 17.5
Mangold / Sugar variety	620	0.3 / 0.3	7.5 / 16.7	7.8 / 17.0

The roots of a table variety of beet and their parts after having grown throughout the vegetation period under the leaves of a sugar beet used as scion showed a sugar content characteristic of the variety. Similar results were obtained with the sugar beet growing under the leaves of a table beet. And if here the sugar content varied between 11.9 and 17.5%, yet the latter figure, characteristic of the sugar beet, should be regarded as more reliable, since the reduced sugar content might be due to the traumatic effect of the operation (which is apt to delay the growth of the root and its storing of sugars), and sometimes to the smallness of the leaf area. The content of re-

ducing sugars in each of the components was also characteristic of the variety it belonged to. New graftings were made in the year 1937 and the estimation of sugars as well as of nitrogen and ash showed the following figures:

Table 2

Chemical Composition of Variously Grafted Beets

Variety	Ash	Total nitrogen	Protein nitrogen	Sugar
	% of dry weight			% of raw weight
Uladovka (sugar beet)	6.2	1.4	1.03	14.3
Bassan (table beet)	12.9	3.3	2.8	6.6
Uladovka / Bassan	14.5	2.52	1.51	6.3
Bassan / Uladovka	8.7	1.52	0.95	11.3

These data agree in general with our former results. We have therefore to conclude that the root tissues of various varieties are specific as regards their ability of storing up sugars. However, the extent of the leaf area is not without influence here. If this is small, the sugar content in the sugar beet is strongly reduced. And some other factors may also be expected to influence the composition of the grafted components if we consider the subject in the light of our conceptions about the processes and functions of the organism as a whole.

In the same year the authors were charged by V. Savitsky, of the Genetic Department of the All-Union Inst. of Sugar Industry, to investigate the question whether the roots or the leaves are the seat of the factors responsible for the low yield of variety *B* 309. They attacked the problem by grafting the leaves of a fodder beet upon the roots of the variety under investigation. The results obtained are presented in Table 3.

Table 3

Chemical Composition (in %) Obtained by Grafting Variety Eckendorf upon *B* 309

Variety	Weight of root in g	Sucrose of raw weight	Reducing sugars of raw weight	Dry matter	Ash	Total nitrogen	Protein nitrogen	Activity of peroxidase
Eckendorf	315	5.0	0.77	8.4	15.4	2.34	1.40	2
B 309	50	9.5	0.11	17.5	9.4	1.75	0.98	
Eckendorf / *B* 309	310	11.6	0.08	18.9	6.3	1.20	0.67	2 / 4

This was a rather clear answer to the question we endeavoured to solve. *B* 309 has a small leaf area. But grafting made the leaf apparatus more powerful and the immediate result was that the roots increased in weight and to a certain extent even in sugars. However, their tissues refused to change in the particulars specific of the variety, as it may be inferred from the activity of the peroxidase. The amount of ash was somewhat reduced in response to grafting. This was certainly because the roots of variety *B* 309 had a rather

high ratio of ash usual for small roots in general, and therefore their increase in weight was naturally attended by a decrease of the ash ratio. An unmistakable influence of the scion upon the stock was thus observed in this type of grafting and this was of a quantitative nature. These graftings were repeated in 1938 and showed essentially the same picture.

Another example of that kind was furnished by grafting Mangold Green (verte à couper), a variety approaching to wild ones, upon a fodder (Eckendorf) and a sugar beet. This was done in the efforts to obtain a new form having Mangold's leaves and Eckendorf's roots. The results are referred to in Table 4.

Table 4

Weight of Root and Sugar Content Obtained by Grafting the Leaves of Mangold Variety upon Various Roots

Variety	Weight of roots in g	Sugar content in %
1938		
Mangold	1000	7.2
Eckendorf		
Mangold	500	18.2
Sugar beet		
Eckendorf	500	4.40
Mangold	170	9.0

The leaves of variety Mangold made the roots of variety Eckendorf increase in weight (600—1200 g) and slightly also in sugars. The reason is that the leaves are retained by the former variety throughout the vegetation period, while in the latter most of the leaves fall as early as during the second half of this phase, and only few are left with the roots.

Till then we had believed that the matter assimilated by variety Mangold is largely used up to strengthen leaf growth. Now we found the leaf apparatus to develop normally and the root to increase in size beyond its usual dimensions. This should be taken to mean that the leaves were working more intensely in the sphere of assimilation. Their sugar content supports this conclusion: 13% in terms of dry matter in Mangold (stillstand in assimilation) about 5% in Mangold/sugar beet (migration and utilization of assimilates) and 3% in Mangold/Eckendorf (enhanced rate of assimilation).

This case suggests a very promising work to be done by genetists: breeding for a better type of beet having the leaves of Mangold and the roots of Eckendorf.

The sugar beet showed a certain increase in sugars after being grafted upon with variety Mangold. Its sugar content was 18.2%, which is somewhat more than usual under similar conditions.

Some experiments of 1938 were run with dwarf beet obtained at the Laboratory of Genetics of the All-Union Inst. of Sugar Industry, by crossing a semisugar with a sugar variety. The quantitative results of those experiments are referred to in Table 5.

The dwarf beet leaves developed much better on the root of the sugar beet than on their own root. In spring, however, they began drying rapidly and soon looked like root's rosettes, by their outward appearance very sug-

Table 5

Weight of Root and Sugar Content in «Dwarf» Graftings

Variety	Weight of root in g	Sucrose in %	Reducing sugars in %
«Dwarf»	15—40	5.2—7.0	0.14
Eckendorf	500	4.4	1.84
Sugar variety	—	12—14	0.05
«Dwarf»			
Sugar variety	150—400	10.7—12.7	0.11—0.16
«Dwarf»			
Eckendorf	200—400	2.7	1.13
Sugar variety	400—500	10.0	0.06
«Dwarf»			
Eckendorf	400—500	7.5—8.2	0.04
«Dwarf»			

gestive of dwarf's rosettes. It would seem that some substance introduced with the foreign root failed to suffice till the end of vegetation. The roots were ranging in weight between 200 and 400 grams, i. e., attained 10—20 times the weight of the dwarf roots. Inverse grafting—of sugar or fodder beet leaves upon dwarf's roots gave both the leaves and roots completely developed. The sugar content of the respective components was above that of the dwarf. And as high an increase in the root weight as several tens of times was also recorded here.

Yet the influence of the scion upon the stock was of a more complicated nature in the case of dwarf grafting. This came to light when we turned to the investigation of the activity of the ferments. Van Overbeck (3) has discovered while studying the usual and the dwarf form of India corn that in the latter the activity of peroxidase and catalase is so high as to destroy the growth hormone and prevent its accumulation in sufficient quantities.

Our investigation* has shown the activity of peroxidase to be only two times higher in the dwarf beet leaves compared to sugar beet leaves grown on the same root. Such increase can hardly be supposed to affect the growth hormone so seriously. The activity of catalase was about the same in all experimental series.

Yet respecting the activity of peroxidase quite different relations were observed in the roots from these graftings (Table 6).

As is seen from these data the varieties tested can be arranged according to the decreasing activity of peroxidase in the order: «Dwarf», Mangold (which is also a form with small roots), sugar beet, fodder beet. The reason that may be put forward to account for the depression of growth in the first two varieties is that the oxidation processes are more intensive in them. It is worthy of note that the enzymatic activity is strongly reduced in the dwarf stocks grafted upon with the leaves of other beet forms (and the root

* One gram of leaf tissue was ground with glass dust and made to 100 cm^3 in volume by adding water. The solution was left to stand with toluene during 14—18 hours; then 1 cm^3 of guayakol (0.1%), 1 cm^3 H_2O_2 (0.1%) and 6 cm^3 water were added per 2 cm^3 of solution. The intensity of the colour was determined after the scale (cobalt nitrate and potassium bichromate) in terms of the milligrams of cobalt.

In determining the activity of catalase 20 cm^3 water were added to 1 g of shredded leaf tissue and 20 minutes later, 10 cm^3 H_2O_2 (0.1%). The data are expressed in terms of cm^3 of evolved oxygen.

Table 6

Peroxidase Activity in Various Series of Experiment

Variety	Activity of peroxidase
«Dwarf»	5—6
Mangold	4
Sugar	2
Eckendorf	1
«Dwarf» / Eckendorf	2
«Dwarf» / Sugar	2
Eckendorf / «Dwarf«	2
Sugar / «Dwarf»	2—3

weight is higher). We undoubtedly meet here with cases of more complicated influence of the scion upon the stock which is obvious from the change in the activity of oxidizing enzymes. The relation to the growth hormone established by van Overbeck may possibly take place here.

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PLANT PHYSIOLOGY

NUMBER OF GRAINS IN A SPRING WHEAT EAR AS DEPENDENT UPON TEMPERATURE AND LIGHT CONDITIONS

By E. I. NESTEROVA

(Communicated by N. I. Vavilov, Member of the Academy, 8.V.1939)

The yield of the spring wheat, as well as of other crops, is determined by the number of spikes per unit area, the number of grains per spike and the weight of a grain.

A spring wheat spikelet is usually found to contain 2 — 3 grains, but it has already been pointed out by Percival(1) while he described the development of a wheat spikelet that as many as 7 — 8 flowers can be set there, but they fail, however, all to develop and many of them succumb.

Hudson (2), Weideman (3) and others have shown by experiment that one of the principal factors in dying away of flowers is the deficiency of mineral supply to the plant. The experiments here described bring into evidence that temperature and light conditions also greatly affect the number of grains per spike and hence the amount of yield.

The experiment was run with two potted speciments of wheat in 1937 and with only one of them (21228 from Italy) in 1938.

Catalogue No	Species and variety	Strain	Origin
21228	*Tr. vulgare suberythrospermum*	Aosta	Italy
25139	» » *milturum*	Aurora	Australia

In the tests of 1937 the plants were given three different temperature treatments while they were passing the period from stalk-formation till heading: «low» temperature (mean daily $t°+8.5°$), «normal» temperature (mean daily $t°$ from $+15$ to 23°) and «high» temperature (22 to 32°). The tests of 1938 were conducted against two backgrounds: «low» temperature (mean daily $t°+6.5°$) and «normal» temperature (15 to 23°) which were adjusted according to the following plan (Table 1).

As is seen from Table 1, the variations in the conditions adjusted involved not only the temperature but the light as well.

Low temperature was secured by early sowing the plants in a hothouse: February 25, 1937 and March 9, 1938. To keep it low as the weather grew warmer, the plants of the respective variants were successively transferred to an unheated hothouse and in the open (early in spring). The plants of the normal series were held in that section of the hothouse where the temperature varied between 15 and 22°C. In the series VI the temperature of the air was always low and the way to increase the soil temperature was by placing the container in a water bath heated electrically. The variant V was kept in the hothouse, the temperature of the soil being reduced by cooling the vessels with running water containing little amounts of ice.

Table 1

Variant	Plant's parts subjected to respective $t°$	Temperature		Light conditions
		by day	by night	
I	Entire plant	Normal	Normal	Natural daylight
	» »	»	»	Shaded with two gauze layers
II	» »	»	Low	Natural daylight
	» »	»	»	Shaded with two gauze layers
III	» »	Low	Normal	Natural daylight
IV	» »	»	Low	» »
V	Roots	»	»	» »
	Aboveground part	Normal	Normal	» »
	Roots	Low	Low	Shaded with two gauze layers
	Aboveground part	Normal	Normal	
VI	Roots	»	»	Natural daylight
	Aboveground part	Low	Low	» »

Results of Experiment. In both of the varieties tested in 1937 those plants showed the highest grain yield which had been subjected to low air temperature while passing the period from stalk-formation till heading (Table 2).

Table 2

Experiments of 1937

Variant	$t°$ during the period from stalk-formation till heading	Number of grains				Grain yield per 10 plants in g	
		in the spike		in the spikelet			
		Aurora	21228 from Italy	Aurora	21228 from Italy	Aurora	21228 from Italy
I	Low	2.15	1.92	26.7	28.7	8.58	14.39
II	Normal	1.67	1.27	16.0	18.6	3.25	7.24
III	High	1.54	0.92	16.6	12.1	5.14	6.59

Experiments of 1938, Spring Wheat No. 21228 from Italy

Variant	$t°$ during the period from stalk-formation till heading	Number of grains per spikelet	Number of grains per spike	Grain yield per 10 plants in g
I	Normal by both night and day . . .	1.19	23.7	15.0
II	Normal by day, low by night . . .	1.40	28.3	14.5
III	Low by day, normal by night . . .	1.13	21.1	9.0
IV	Low by both day and night	1.54	30.1	17.2
V	Roots under low $t°$, aboveground parts under normal $t°$	1.09	21.0	11.3
VI	Roots under normal $t°$, aboveground parts under low $t°$	1.48	29.7	16.5

From the data of spike analysis (1937) referred to in Table 2 it will be obvious that the highest yield of grain was a result of the increased number of grains both in the spikelet and in the spike. The variety 21288 was especially liable to respond in that way to the influence of temperature and did not remain indifferent to this factor even while in the period of flowering. Thus, when the temperature was +23° by day and +10° by night 60% of the developed flowers set grains, while only 49% of them did so when the temperature varied betwen 20 and 27°, and this ratio dropped to 37% when the temperature was kept between 20 and 32°.

The experiments of 1938 have shown that the number of grains in a spike of the spring wheat 21228 can be increased not only by keeping the temperature low throughout 24 hours, but it will suffice to reduce it at night. Heating of the soil when the temperature of the air was low remained without influence on the number of grains per spike, while a respective cooling at normal air temperature made the number of grains per spike to decrease.

Light conditions proved of utmost importance as regards the number of grains in a spike. The plants shaded by two layers of gauze had both the number of grains per spike and the grain yield considerably reduced as compared to controls given natural daylight (Table 3).

Table 3

	Variant	Number of grains per spikelet		Number of grains per spike		Grain yield in g	
		Natural daylight	Shading	Natural daylight	Shading	Natural daylight	Shading
I	Normal $t°$ throughout 24 hours	1.19	0.83	23.7	17,0	15.0	7.9
II	Normal by day, low by night	1.40	1.06	28.3	18.0	14.0	8.6
III	Roots under low $t°$	1.09	0.56	21.0	11.5	11.3	4.5

The weight of 1000 grains was reduced from 57 to 49 g by the shading applied in the period previous to heading.

The chemical composition of the grain was found to change if the temperature continued low from the time of stalk-formation until heading. Under these conditions as shown by the data obtained by M. A. Deshevova which are summarized in Table 4, the protein ratio ($N \times 5.70$) in a wheat grain is considerably reduced.

Table 4

Protein Ratio in a Wheat Grain

$t°$ in the period from stalk-formation till heading	Fertilized		
	Previous to sowing	While coming into stalk	While coming into ear
High	19.55	20.35	20.10
Low	14.80	15.25	21.6

If, however, the plants while coming into ear were supplied with full rations of mineral fertilizers, the quality of their grain was saved from unfavourable influence of low temperature.

Mention needs also to be made of how the length of the period between stalk-formation and heading was affected by temperature. In the experiment

of 1937 the varieties No 21228 and Aurora came into ear 18 days and 16 days later respectively if the temperature continued low, compared to their heading at normal temperature.

In the experiment of 1938 delayed heading was brought about by decreasing the temperature only by day or only by night. This delay was reduced by 4 days if the soil under the experimental plants was heated. When shaded with gauze, the plants came into ear 5—6 days later compared to natural daylight controls.

Favourable effect of reduced temperature upon the number of grains per spike appears to be due to the enrichment of plants with soluble carbohydrates ([4], [5]). The increase in the latter is conducive to a better utilization of mineral elements as well (indirect evidence furnished by our experiments in favour of this fact is that the reaction of plants to mineral nutriment was enhanced by low temperature). On this assumption an estimation of carbohydrates in plants grown at varying temperatures was made in 1938. The results of the analysis showed the amount of soluble carbohydrates to increase 2—3 times at low temperature, the share of the sucrose in this increase being exceptionally great (Table 5).

Table 5

Mean daily $t°$	During	Fertilizer	Leaves, % of abs. dry weight			Stems, % of abs. dry weight		
			Glucose	Sucrose	Total sugars	Glucose	Sucrose	Total sugars
+ 6°	6 days	O	3.73	13.42	17.14	2.79	9.60	12.39
+17°	6 »	O	2.40	3.80	6.20	1.85	6.92	8.77
+ 6°	16 »	O	4.02	15.06	19.08	3.86	13.72	17.58
+ 6°	16 »	NPK	4.03	17.07	21.10	3.41	12.05	15.46
+17°	16 »	O	2.59	5.58	8.17	1.52	3.37	4.89
+17°	16 »	NPK	2.36	3.77	6.13	1.70	2.18	3.88
+ 6°	21 »	O	4.92	12.47	17.39	3.26	10.03	13.29
+ 6°	21 »	NPK	4.42	11.26	15.68	3.78	12.17	15.95
+17°	21 »	O	2.66	5.40	8.06	2.88	4.66	7.54
+17°	21 »	NPK	3.15	5.25	8.40	2.38	2.71	5.09

From the aforesaid it follows that under the conditions of our experiments the delay in growth and development of the spike due to reduced temperature was concomitant to the increase of plants in carbohydrates, and this resulted both in a vigorous growth of vegetative parts and in an increased number of grains per spike. The conditions of carbohydrate supply changed for the worse with the increase in temperature and the result was a reduced number of grains per spike. These results fall in line with the data obtained on shading the plants with gauze variety 21288 from Italy (Tables 6 and 2).

Table 6

Variant	Light conditions	Date of sampling	Leaves, % of abs. dry weight			Stems, % of abs. dry weight		
			Glucose	Sucrose	Total sugars	Glucose	Sucrose	Total sugars
I	Natural daylight		3.01	2.87	5.88	2.56	3.74	6.30
	Shading	21.V	2.05	2.42	4.47	1.70	1.88	3.58
II	Natural daylight		3.75	3.12	5.87	2.29	3.22	5.51
	Shading	21.V	2.01	3.05	5.06	1.50	2.85	4.35

Conclusions

The number of grains in a spike of spring wheat is greatly affected by both temperature and light conditions prevailing during the time when the plant is making its progress from stalk-formation to heading.

If the temperature at that period is reduced to +8°, the plant by increasing in soluble carbohydrates (glucose and especially sucrose) makes stronger vegetative growth and forms more grains in the spikes and hence its yield is increased. It is when the temperature is lowered at night that this effect is especially strong.

The reverse is the case when the temperature is raised or the plants shaded with gauze during the period from stalk-formation till heading.

The conclusion to be drawn from the relationship established in our experiments between the number of grains per spike and the accumulation of carbohydrates is that the conditions of supply are a potent factor in the development of generative organs of a wheat flower. Moreover, we have to emphasize the great importance of early sowing the spring wheat, since this makes it to suffer low temperature, especially at night, while it is passing from stalk-formation to heading.

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AGROPHYSIOLOGY

QUALITY OF GRAPE YIELD AS AFFECTED BY ACCELERATED DEVELOPMENT

By J. I. POTAPENKO and N. V. NOVOPAVLOVSKAYA

(Communicated by A. A. Richter, Member of the Academy, 15. V. 1939)

Southern crops cannot be moved farther north unless their vegetation period is shortened and this may be done both through changing the nature of plants and by agrotechnical means.

In the case of grape culture spring frosts are a great danger and stand as a serious obstacle in the way of the plant to more northern latitudes. To Michurin belongs the credit for having suggested to surmount this obstacle by shortening the vegetation period of the vine.

The biology of fruit-plant development has been investigated by the present authors on the basis of theoretical considerations put forward by Michurin and Lyssenko, and the result is a new method for shortening the vegetation period with the help of agrotechnical measures, which makes it possible successfully to strive with spring frosts while growing the grapes in the northern regions and to enhance the yield.

The essential of this method is the adjustment of suitable temperature and light conditions. The latter can either slow down or speed up the development of the plant which is not indifferent to their action while it is passing the vegetation period (at Michurinsk). With a long day and reduced temperature during the first half of this period the development of the grape vine is retarded whereas it is accelerated if the day is reduced and the temperature favourable. The technique by means of which we succeeded to shorten vegetation and speed-up development was to leave reserve shoots along with the usual ones on each of the shrubs.

In spring after the grape shrub was freed from the earth cover, part of the shoots, the reserve ones, were prostrated in the earth at a depth of 15 cm. Soil was largely the cover of the reserve shoots. Organic matter (straw, leaves, etc.) was partly used as cover too and since the results were positive its use will be tried once more in the future. The organic covering on the soil surface was extended over the reserve shoots only lest the entire area of the plot should be subject to cooling. The reserve shoots were freed from the earth cover 15—20 days after the usual shoots had begun vegetation. Thus, if the vine buds started swelling at Michurinsk between April 25 and May 1, the reserve shoots were dug up between May 15 and 21 respectively, i. e. when the danger of frost was over.

Due care was exercised while taking up the reserve shoots to prevent breaking off the buds which had attained in the earth a length of 1.5 to 2 cm.

Should the weather be clear and hot when the reserve shoots are being freed from the soil, their buds can get scorched by the sun if the shoots are left to lie on the surface. Therefore the reserve shoots when free from the soil cover were at once attached to stakes of a wire trellis.

Further on they were cared for in the usual way.

If the frosts failed to occur during spring time the reserve shoots served to increase the yield because their flowering was shifted towards a warmer period and this was conducive to a better formation of ovaries and to a higher yield. Thus in 1938 at the Michurin Central Genetic Laboratory the variety Malengra Seedling from Michurinsk gave a yield on the reserve shoots which was twice that on the usual shoots.

If one had to do with a variety which required another for pollination, the reserve shoots of both of them were laid in the earth.

Fig. 1. Shrub of Melangra Seedling. Left, control shoots, freed from earth cover April 25 1938. Right, reserve shoot taken up May 17 1938.

If the reserve shoots were dug up later this was not followed by a respective delay in ripening. The latter was found to be practically simultaneous in the experiments conducted under field conditions with a number of varieties from both Michurinsk and Europe in the years 1936, 1937 and 1938.

From the data on the mechanical and chemical composition of vine berries from the control and the reserve shoots it is evident that the average weight of a grape is higher in the control than in the reserve shoots. The same is true of the flesh/seed weight ratio with the exception of two varieties Malengra Early and Muscat Lunel where it is higher in the reserve shoot grapes.

Yet in spite of the smaller size of the fruit not only can the yield of the reserve shoots be equal to but it may even be higher than that of the control shoots, as it is in the case of Malengra Seedling.

Comparative chemical analysis showed 6 of the 10 varieties tested to have their sugar content and sugar acid ratio higher in the reserve than in the control shoots; Malengra Seedling, Madelaine Angevin, Malengra Early, Black Sweet, Shaslia Muscat, Muscat Lunel, while the reserve was the case with the four other varieties Rose Shaslia, Rose Muscat, Metallic and Golden Ray.

The cause of the different behaviour of the varieties is that in six of them, which had their sugar content higher in the fruit of the reserve shoots, the latter after being dug up from the earth shared with the control shoots the same conditions of light and temperature being attached in a suitable manner to a wire trellis or stakes throughout the vegetation period. In the second group of varieties, however, the reserve shoots were in less favourable conditions of light and temperature compared to the control shoots. This was partly because they were smaller in length and also because the shoots stood very close to each other and the experimental vines were shaded by the control ones which sent forth shoots intensively.

The conclusion to be drawn from this data is that the reserve shoots if

grown under equal condition of light and temperature not only can produce ripe fruit simultaneously with the controls, but they can also give higher yield with respect to the content of sugars and the sugar acid ratio.

And since the increase in sugars, the decrease in acids and the enhanced sugar acid ratio point to the fact that a new developmental phase has set

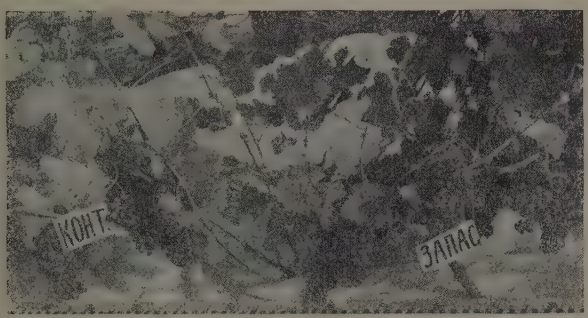

Fig. 2. Shrub of Shaslia Rose. Left, yield of a control shoot freed from earth cover April 25 1938. Right, yield of the reserve shoot taken up from the earth May 17 1938.

in to relieve the vegetation period, this is a further evidence in favour of the accelerated development of the reserve shoots.

The technique suggested is very simple and as it does not involve any risk in the practical work it is worth while to try it in other localities.

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AGROPHYSIOLOGY

EXPERIMENT ON GROWING THE SOUTHERN DEGENERATED POTATO IN THE MIDDLE BELT OF THE USSR

By A. K. EFEIKIN

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In a large part of the southern territory of the USSR the cultivation of potato was long being hindered seriously by the fact that a running out or degeneration of this crop eventually resulted from reiterated reproduction of local seed material ([1-6]). Not until the last years and until Lyssenko suggested the summer planting of potato in the south, was the problem met and the continual reproduction of non-degenerated seed material became possible there([2-4]).

Three theories have been put forward to account for the degeneration of potato in the south.

The first suggests that some virus is here the responsible cause. It has, indeed, been established that potato is liable to be so affected, and Rischkov([7]) has described about 30 virus diseases attacking it. Nevertheless, no experimental investigation has ever proved the virus nature of the southern degeneration.

The second theory ascribes the responsibility for degeneration to some poisonous substances which are supposed to accumulate in potato in the course of metabolism under the influence of high temperature prevailing in the south. Of special importance for this theory are the works of Altergot([8]). The latter has proved by experiment that under the influence of high temperature the trend of biochemical processes in a vegetable cell is towards accumulation of ammonia which acts as a poison upon the living protoplasm. The result of this course of metabolism is that the cell, despite general claims to the contrary, is killed by autointoxication with ammonia long before the coagulation of the protoplasm. Special investigation by Rakitina and Shumova([9]) have shown that the effect of high temperature on potato is to increase the rate of respiration sharply, to further the formation of the products of anaerobic metabolism (C_2H_5OH, CH_3CHO), to reduce the content of amides and to enhance the formation of ammonia.

If the temperature continues high, the biochemical changes are attended by distinct morphological symptoms of degeneration, and therefore the above authors come to the inference that «an enhanced rate of brake-down processes is one of the features characteristic of the southern degeneration of potato».

Quite peculiar is the interpretation advanced by Lyssenko([2]). Starting from the principles of his phasic development theory, he explains the degeneration of potato in terms of its phasic ageing which takes place in the growing point meristem of sprouts and buds in the eyes under the influence of high temperature during tuber formation. According to Lyssenko, neither diseases nor any

other abnormal processes are responsible for the degeneration of potato, but he considers it a natural result of this plant's phasic development. And inasmuch as the changes occurring in the course of phasic development are irreversible, irreversible, too, is the degeneration. The task which I have set before myself was to clear up the question, what changes will take place in the degenerated plants of potato if they have been moved back to the north. This being established, considerable light will be thrown upon the nature of degeneration.

The work was carried on in the Chuvash Agricultural Institute (Cheboksary), 56°7′ N. l. in 1937—1938. The material tested consisted in about 2 kg of degenerated tubers, variety Epicur, supplied by the Odessa Institute for Genetics and Plant-Breeding, 46°40′ N. l. The controls were the tubers of the same variety received from Pushkin, 59°38′ N. l. In what follows the terms «northern» and «southern» refer to the plants from the tubers obtained from Odessa and Pushkin, respectively.

The tubers were planted directly in an open border. In the experiments of 1937 the seedlings appeared above ground 32 days after planting, June 13, from both southern and northern material simultaneously. All seedlings made their appearance at once. But the southern plants became different from the northern plants after the first days of development. The northern potato developed vigorous branchy stems with broad leaves, while in the southern potato the stems were low, thin, poorly branched, and bore small curly leaves whose colour was more dark-green compared to the northern plants. Flowering set in July 11, 28 days after germination, in both kinds of plant simultaneously. This fact of simultaneous flowering is worth consideration. On the concept of Lyssenko, the southern degenerated plants are more advanced in age phasically compared to the northern plants, and should therefore be expected to start flowering when the latter have yet to pass earlier stages. This implication of the theory is at variance with the fact of simultaneous flowering. If germination and flowering set in simultaneously in the southern and in the nothern plants, nevertheless, the above-ground green parts began drying off earlier in the former than in the latter, and toward the end of August they were completely dry. In the northern potato complete dryness was observed 15—17 days later. Harvesting was done September 13, after the aerial organs died away in the northern plants.

The whole harvest was left to be planted in the year 1938. In order to take account of the influence which the size of the tubers is apt to exert upon the development of plants from them, all the southern tubers were divided into three sets by weight: I—25 to 50 g and more; II—10 to 25 g; III—4 to 10 g, and the same was done with the northern tubers from Cheboksary. Planting was done May 15. In set I the first southern seedlings appeared above ground June 5; the northern ones, June 6. The respective dates for set II are June 6 and 9. In set III the first appearance of seedlings took place simultaneously on June 6. But in all of the sets the bulk of seedlings made their appearance two—three days later in the northern than in the southern potato. During their first growth the northern and the southern seedlings were much alike with regard to habitus. The curliness of leaves characteristic of degenerated potato had disappeared almost entirely. During further development, however, the difference between the two lines under test became increasingly manifest. The southern plants started flowering July 6, while the northern plants did this July 8. The aerial organs of the former began drying away in the second decade of August, i. e. 8—9 days earlier compared to the northern line, while this difference was 15—17 days in the experiment of 1937.

At the time of harvesting (September 9) two most vigorous shrubs from set III of the northern line had their aerial organs not entirely dry, and their

tubers were found to have strongly sprouted. Some of the sprouts appeared above ground to form small green leaves. This phenomenon is not usual in the region of the experiment and should, probably, be ascribed to the exceptionally hot and dry summer which prevailed that year. The fact is worth mentioning, since the sprouting of new tubers while still in the ground is a symptom of southern degeneration, and, curiously enough, in our experiment no one of the southern plants was observed to have sprouted tubers.

The most thorough comparison of the lines tested involved the following characteristics: 1) average weight of a tuber, 2) number of tubers per plant (all the tubers set were taken into account), 3) yield weight per plant, 4) number of stems per shrub and 5) average height of the plants.

The obtained data showed that the increase in the weight of a tuber was from 14.6 to 38.1 in set I, and to 44.8 in set III of the southern degenerated potato from Odessa after it had been reproduced in a more northern region during two consecutive years; i. e. it has reached three times its original weight and surpassed the average weight of a northern tuber, whose variation during this time was so insignificant as not to cross the limit of the experimental error. The set II was intermediate with respect to all the characteristics, and nothing new would be about the question if we were to consider these data. As to their outward appearance, the northern and the southern line failed to show any appreciable difference during their second year in Cheboksary. At the first glance it is difficult to see why the average weight of tubers in the plants of set III grown from small tubers should be higher than it was in set I, in which the plants had been grown from large tubers. The reason, however, is that the number of tubers per plant is lower in set III.

The number of tubers per plant increased 1.5 time in the southern line within the two experimental years, while it remained unchanged in the northern line. The increase in the tuber yield per plant during the same period was 4 times in the southern line and quite insignificant in the northern line. The number of stems per plant increased 1.5 time in the former and showed no increase in the latter. The southern plants were also 25% taller compared to their original height. The conclusions to be drawn from the above data are as follows:

1. If the southern degenerated potato has been moved into more northern latitudes, the symptoms of degeneration disappear gradually until the plant restores all its normal specific and varietal characters. The implication of this fact is that degeneration of potato is a reversible process.

2. Biologically the southern degeneration of potato is a slow modification which appears to be due to some toxic substances (ammonia and others) which, as shown by Rakitin and Shumova ([9]), show a tendency to accumulate in the plant in the course of abnormal metabolism if the temperature continues high. When the cause responsible for the formation of these poisonous substances is removed, the symptoms of degeneration naturally disappear.

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EXPERIMENTAL MORPHOLOGY

REGULARITIES IN GROWTH OF CHICKEN EMBRYOS

By I. J. PRITZKER

(Communicated by I. I. Schmalhausen, Member of the Academy, 17. VII. 1939)

The aim of the present work was to establish certain regularities in the growth of chicken embryos under combined higher and lower incubation temperatures and ascertain to what extent growth compensation may take place at different combinations of temperature.

Inasmuch as the natural periods of growth of the chicken embryo have not been sufficiently ascertained, the incubation periods during which we have applied differentiated temperature effects were taken by us arbitrarily: we have studied the effect of a combination of temperatures on the growth of chicken embryos in periods of six days. This is, of course, an arbitrary division, but with a certain approximation it offers the possibility of obtaining an answer to the question which interests us. We have chosen this division because in artificial incubation the change of regime according to technical instructions likewise takes place in periods of six days, as, for instance, in the Spartak incubator. In addition it was of interest to learn about the growth of the chicken embryo under a differentiated combination of temperatures by the time the eggs are transferred to the nursery trays, i. e., after a lapse of 18 days of incubation.

In order to find an answer to these questions we have made two series of experiments. In the first case a temperature of 40° was maintained throughout two six-day periods and 37° during one six-day period. In the various sets of experiments of this series the lower temperature respectively fell on the first, second and third six-day incubation period. In the second series, a temperature of 37° was maintained throughout two six-day periods and 40° during one six-day period. In this series the higher temperature likewise fell on each of the three six-day incubation periods.

The experiments were made with a Stephens 400-eggs two-chamber incubator. In one of the chambers a temperature of 40° was maintained and in the other 37°. The temperature combinations were effected by a transfer of the eggs for a corresponding period from the chamber with 40° to the chamber with 37° and vice versa.

White Legghorn eggs, laid within the last three days and collected on the same day in one and the same poultry yard, were used for the experiments. The eggs were opened and the embryos weighed respectively after a lapse of 6, 12 and 18 incubation days. After a elapse of 6 days the embryos from the 37° chamber weighed on the average (in both series of experiments) 0.26 g

while those from the 40° chamber, 0.59 g. The weight of the embryos after 12 incubation days is shown in Table 1.

Table 1

Effect of Different Temperature Combinations (37° and 40°C) on Weight of Embryos after 12 Days of Incubation

Number of embryos	Temperature		Mean weight of eggs before incubation, in g		Mean weight of embryos			
					in g		% of weight of eggs	
	1st six-day per.	2nd six-day per.	1st exp.	2nd exp.	1st exp.	2nd exp.	1st exp.	2nd exp.
22	40	40	54.68	56.0	6.31	6.74	11.54	12.03
21	40	37	55.37	55.8	4.51	4.98	8.14	8.92
20	37	40	55.00	56.6	3.55	4.48	6.41	7.90
23	37	37	55.06	56.4	3.44	3.54	6.25	6.27

From Table 1 it may be seen that the greatest weight was attained by the embryos which were developing all the time under 40°. Second place in weight is held by the embryos which during the first six days were kept in the 40° chamber and the following six days in the 37° chamber. Third place in weight is held by the embryos which were developing under a reversed order of the two temperatures. Lastly, the fourth place is held by the embryos which all the 12 days were developing under 37°. The following new regularity became manifest in this case. While the sum total of temperatures was the same in the first and second groups, the embryos which were developing under a higher temperature during the first six days showed greater weight than those which were developing under a higher temperature the second six days.

Data as to the weight of 18-day embryos which were developing under methodically varying temperature combinations are given in Tables 2 and 3.

In the case of 18-day embryos those which were all the time developing under 40° showed the greatest weight, while those which were all the time developing under 37° showed the lowest weight. As to those which for two six-day periods were developing under 37° and one six-day period under 40°, they all occupied places between the first and last, their weight being the greater, the nearer the six-day period during which they were developing under 40° approximated the beginning of the incubation (Table 2).

Table 2

Effect of Higher Temperature at Various Stages of Incubation on Weight of 18-Day Embryos

Number of embryos	Temperature			Mean weight of eggs before incubation, in g		Mean weight of embryos			
						in g		% of weight of eggs	
	1st six-day per.	2nd six-day per.	3rd six-day per.	1st exp.	2nd exp.	1st exp.	2nd exp.	1st exp.	2nd exp.
22	37	37	37	55.52	56.3	18.72	19.47	33.72	34.58
20	37	37	40	54.75	56.1	19.0	20.09	34.70	36.07
21	37	40	37	54.43	56.1	20.31	22.19	37.59	39.56
18	40	37	37	54.47	56.8	22.37	22.55	41.07	39.70
23	40	40	40	55.47	56.3	25.26	25.63	45.54	45.52

The same regularity is manifest in Table 3. Eggs which in the main were developing under 40°, but for one six-day period were kept under 37°, showed the greater weight, the farther from the beginning of incubation this six-day period was.

Table 3

Effect of Lower Temperature at Various Stages of Incubation on Weight of 18-Day Embryos

Number of embryos	Temperature			Mean weight of eggs before incubation		Mean weight of embryos			
						in g		% of weight of eggs	
	1st six-day per.	2nd six-day per.	3rd six-day per.	1st exp.	2nd exp.	1st exp.	2nd exp.	1st exp.	2nd exp.
23	40	40	40	55.47	56.3	25.26	25.63	45.54	45.52
19	40	40	37	54.84	56.0	23.66	23.90	43.14	42.67
16	40	37	40	55.23	56.1	20.70	22.06	37.47	39.32
23	37	40	40	54.66	56.3	20.27	21.64	37.08	38.43
22	37	37	37	55.20	56.3	18.72	19.47	33.72	34.58

Both series of experiments having been conducted simultaneously, the groups which were developing under 40 and 37° serve as a control to both of them. The data obtained for both series of experiments were treated in accordance with the methods of Mainot and Schmalhausen and are also accompanied by figures showing increase in weight in grams (Tables 4 and 5).

Table 4

Increase in Weight of Embryos Under a Temperature Set Higher at Various Stages of Incubation (Increase in grams and %)

Temperature			Weight on 6th day in g	12th day				18th day			
1st six-day per.	2nd six-day per.	3rd six-day per.		Weight in g	Increase in g	% of incr.	Constant of growth (accord. to Schmalhausen)	Weight in g	Increase in g	% of incr.	Constant of growth (accord. to Schmalhausen)
37	37	37	0.26	3.44	3.18	1 323.0	3.78	18.72	15.28	544.2	4.20
37	37	40	0.26	3.44	3.18	1 328.0	3.78	19.0	15.56	552.3	4.35
37	40	37	0.26	3.55	3.29	1 366.0	5.05	20.31	16.76	570.9	4.20
40	37	37	0.59	4.51	3.92	764.6	3.06	22.37	17.86	496.0	3.90
40	40	40	0.59	6.31	5.72	1 069.4	3.51	25.26	18.95	400.6	3.30

The results produced by both experiments are so close that on their basis one may draw quite definite conclusions.

The growth of the embryos, at least in the first three six-day periods, depends not only on the sum total of temperature, but also on the way the temperature is distributed among the various periods of incubation. The sum total of temperature being equal, the weight of the embryos which in the main were developing under 37° was all the heavier on the 12th or 18th day of incubation, the earlier the change to 40° was effected, and vice versa, the weight of the embryos which in the main were developing under 40° were all the lighter, the earlier change to 37° was effected.

Table 5

Increase in Weight of Embryos Under a Temperature Set Lower at Various Stages of Incubation (Increase in grams and %)

Temperature			Weight on 6th day in g	12th day				18th day			
1st six-day per.	2nd six-day per.	3rd six-day per.		Weight in g	Increase in g	% of incr.	Constant of growth (accord. to Schmalhausen)	Weight in g	Increase in g	% of incr.	Constant of growth (accord. to Schmalhausen)
40	40	40	0.59	6.31	5.72	1 069.49	3.51	25.26	18.95	400.6	3.30
40	40	37	0.59	6.31	5.72	1 069.49	3.51	23.66	17.35	374.26	3.15
40	37	40	0.59	4.51	3.92	764.40	3.06	20.70	16.19	458.98	3.60
37	40	40	0.26	3.55	3.29	1 365.38	5.05	20.27	16.72	470.98	4.20
37	37	37	0.26	3.44	3.18	1 323.07	3.78	18.72	15.28	544.2	4.20

These regularities were observed by us twice and were mutually confirmed in both series of experiments.

The younger the embryo, the more rapid their growth response to the effect of a higher temperature (but not a too high one). In regard to the rate of growth, the application of a higher temperature at the later stages of incubation fails to give such an effect as a higher temperature applied in the earlier stages of incubation.

Our data show that van't Hoff's law ceases to be true not only beyond certain limits of temperature approaching the optimal, but also beyond certain age limits in the case of embryos of birds (and probably not only of birds). This once more confirms the hypothesis that embryos of oviparous vertebrata show certain properties which enable them positively to react to outside temperature effects, and also that such properties are the more sharply expressed, the older the embryo.

Hence such facts as compensation during the growth of the embryo: retarded growth in earlier periods of development is compensated by a more rapid growth in subsequent periods and, vice versa, an accelerated growth is compensated towards the end of the incubation by a retarded growth. Table 6 shows that this is what takes place to an even greater extent after the 18th day of incubation. Thus, after 18 days of incubation the rate of growth under 37° is both relatively and in absolute figures much higher than under 40°.

Table 6

Indices of Growth of Embryos after 18 Days of Incubation under Hyperthermia (40°) and Hypothermia (37°) (Weight in g)

Temperature	Wt. on 18th day	Wt. of chick one day old; without yolk	Increase in g	Incubation period in days	Number of days before chick is hatched	Mean daily increase in weight after 18th day of incubation	
						in g	% of growth
37	18.72	32.53	13.81	22	4	3.45	18.43
40	25.26	29.59	4.33	20	2	2.16	8.55

Many attempts have been made in recent years by research workers in the field of incubation to establish a «standard» of development of embryos of birds. It is assumed that by comparing the growth of embryos in the incubator with the «standard» it may be possible to introduce the respective corrections in the regimen of incubation. However, all these attempts proved fruitless. Thus, Romanov (1) analyzed the curves of growth of chick embryos as given by various writers (Volk, 1885; Liberman, 1888; Hasselbach, Lamson and Edmond, 1914; Murrey, 1925; Mitchel, Hamilton and Card, 1926; Schmalhausen, 1926; Anderson and Brodie, 1927) and came to the conclusion that they are very difficult to compare.

In the light of our data this is easily understood. Difference in the temperature applied in artificial incubation cannot but cause difference in the rate of growth of the embryos.

All this makes it purposeless to attempt to establish a single «standard» of development for embryos of all stocks of fowl, to be valid in all seasons, in all incubators under all conditions of incubation. At the same time, however, the accumulation of material on the growth of embryos of various kinds of poultry is undoubtedly of practical import. With the knowledge of the curves of the embryonic growth of particular varieties of poultry under given conditions of incubation as well as of the general regularities of embryonic growth, it will no doubt be possible within the nearest future to include growth of embryos among the criteria for biological control of incubation.

Conclusions

1. The effect of one and the same sum total of incubation temperature on the rate of growth of embryos may vary depending on the sequence in which the changes of temperature follow each other.

2. The effect of a change to a higher temperature maintained during a fixed period of time is all the greater in stimulating growth, the earlier such change is made. And likewise the effect of a change to a lower temperature maintained during a fixed period of time is all the greater in retarding growth, the earlier such change is made.

3. A more rapid growth of the embryo in the earlier stages of its development is compensated by a somewhat retarded growth in the later stages. And, vice versa, a retarded growth at the beginning of the incubation is compensated by a more rapid growth at the end of the incubation.

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EXPERIMENTELLE MORPHOLOGIE

WACHSTUM UND VERWANDLUNGEN IN GEWEBEKULTUREN DES PERZEPTORISCHEN BLATTES DER NETZHAUT

Von J. A. VINNIKOV

(Vorgelegt von I. I. Schmalhausen, Mitglied der Akademie, d. 17. VII. 1939)

Die vorliegende Arbeit schliesst eine Reihe von Arbeiten des Verfassers ab, welche den retinalen Blättern des Augenbechers gewidmet sind ([1-4]). Als Ausgangsmaterial für die Untersuchung dienten Augen von Kaninchen im Alter von 15 Tagen des intrauterinen Lebens und später, sowie neugeborener Kaninchen bis zum 20-ten Lebenstag, d. h. schon gut sehender Tiere.

Bie dem Kaninchen bleibt die Einteilung in eine äussere und innere Kernschicht auf den frühen Embryonalstadien noch aus. Früher als die übrigen, erscheinen die gangliöse Schicht und die innere Netzschicht. Es wird eine aktive mitotische Tätigkeit der kambialen Elemente der sogen. neuroepithelialen Schicht, die dem Pigmentblatt anliegt, beobachtet. Die Mitosen hören erst am 3—4 Tage nach der Geburt auf. Vor der Geburt des Tieres entsteht die innere Kernschicht, mit sämtlichen neuronalen Elementen, und die äussere retikulare Schicht. Das Auftreten von Nervenelementen, die miteinander in Verbindung treten, geht vor sich zugleich mit der Entwicklung der Müllerschen radialen Fasern, welche die Grundlage der Gliakomponent der Netzhaut bilden. Die Müllerschen Fasern bilden auch die membranae limitantes externa et interna der Netzhaut. Die sich intensiv teilenden Elemente der äusseren Kernschicht zeichnen sich durch ihre tiefere Färbung und die characteristische Kernstruktur aus, welche in dem besonderen Bau und in der besonderen Einteilung des Chromatins Ausdruck findet. Aus den Zellen der kambialen Schicht der Netzhaut bilden sich nach der Geburt die Sehelemente mit besonderen Segmenten—Stäbenen und Zapfen. In der differenzierten Netzhaut werden zuweilen auch intensiver sich färbende Glia- und Nervenelemente nachgewiesen. Die Eigentümlichkeiten des Kernbaues und die tiefere Färbbarkeit des Protoplasmas der Elemente der äusseren Kernschicht bleiben während des ganzen Lebens beibehalten und stehen bei dem erwachsenen Tiere, allem Anschein nach, mit den funktionellen Eigentümlichkeiten in Zusammenhang. Die Bildung der Müllerschen und anderen Stützelemente der Netzhaut lässt sich nur mit Mühe verfolgen. Sie werden erst nach dem Erscheinen eines characteristischen fibrillären Baues in ihrem Zytoplasma merklich. Bei einer gewissen Geübtheit gelingt es die Kerne der Müllerschen Fasern, die im Zentrum der inneren Kernschicht gelegen sind, ihrer Form und Struktur nach zu verfolgen.

Die Veränderungen des beschriebenen Ausgangsmaterials wurden bei der Gewebezüchtung sowohl in vivo, als auch auf einer grossen Zahl fixierter Präparate in 142 Versuchsreihen, im Laufe von 3 Jahren beobachtet. Die

Explantationszeit ging über 48 Tage hinaus. Die in einen Hängetropfen aus dem Nährboden gebrachten Netzhautstückchen rufen eine äusserst intensive Fibrinverdünnung hervor. Schon nach 24 Stunden rundet sich das im flüssigen Plasma frei flotierende Explantat ab und verwandelt sich in ein hohles Bläschen. In einem derartigen Bläschen sind die Elemente der Stäbchen und Zapfen nach aussen, die gangliöse Schicht aber nach innen gewendet. Diese Bläschen verhalten sich verschieden, in Abhängigkeit von dem Differenzierungsgrade des Ausgangsmaterials. Die embryonalen Explantate fahren fort sich auf kosten der sich intensiv vermehrenden Elemente der äusseren Kernschicht zu differenzieren, bis zur Bildung der äusseren und inneren Segmente der Stäbchen und Zapfen, sowie der Müllerschen Fasern. In den Bläschen aus dem stärker differenzierten Ausgangsmaterial bleibt die histologische Struktur im Laufe der ersten 24 Stunden ohne merkliche Störung.

Die Bildung der Bläschen aus den Netzhautexplantaten, die lange leben und sich lange entwickeln, kann mit den allgemeinen regulativen Fähigkeiten des Augenbechers ([5]) nicht in Zusammenhang gestellt werden. Derartige Explantate können als «Äuglein» bezeichnet werden.

Nach dem zweiten Tage werden in der das «Äuglein» bildenden Netzhaut interessante Umwandlunden nachgewiesen, die im Vergleich zur normalen Ontogenese in gerade entgegengesetzter Richtung verlaufen. Diese Erscheinung wurde ihrerzeit auch für andere Teile der retinalen Blätter der Netzhaut beschrieben. Ein beträchtlicher Teil der Zapfen- und Stäbchenelemente geht zugrunde, besonders an den Stellen, wo die Mb. lim. ext. geschädigt ist. Die äusseren und inneren Segmente der Stäbchen und Zapfen unterliegen einem lamellären Zerfall. Der Körper der Zellen selber schwillt an und an der Stelle des früheren Segments wird häufig die Bildung einer feinen Nervenfaser mit characteristischen Wachstumszapfen am distalen Ende nachgewiesen. Derartige neugebildete Fasern können durch die Löcher in der Mb. lim. ext. ins Fibrin eindringen. Sie sind sowohl in vivo, als auch auf Präparaten, die mit Methylenblau gefärbt und nach Champy fixiert sind, gut sichtbar. Derartige Fasern leben nicht mehr, als 2—3 Tage, wachsen niemals auf eine grosse Strecke vor, sie sind äusserst zart und bilden sehr selten Verästelungen und Anastomosen. Die Bildung von Nervenfasern an der Stelle der früheren inneren Segmente lässt sich meistens am Material von alten Tieren verfolgen. Die für einige Zeit stehen gebliebenen Mitosen in der äusseren Kernschicht kommen wieder in einer grossen Zahl zum Vorschein. Die intensive Vermehrung der Stäbchen- und Zapfenelemente führt zum Eintritt von neuem Zellmaterial in die innere Kernschicht und verändert die Struktur der letzteren. Andererseits lässt sich auf denselben Explantationsstadien an den Stellen der Risse der Mb. lim. ext. die Verschiebung der sich aufeinander häufenden, verändernden Elemente der äusseren Kernschicht ins Fibrin, mit der Bildung in derselben einer umfangreichen Wachstumszone, verfolgen.

Die Veränderung der inneren Kernschicht und der gangliösen Schicht geht zugleich vor sich. Die gangliösen Elemente weisen eine Regeneration der Nervenfortsätze und eine Neubildung der Nervenfasern auf. Die Nervenfasern wachsen weit ins Fibrin ein und durchdringen das Stückchen und die Wachstumszone ringsumher. Auf den nach Cajal behandelten, sowie auf den Methylenpräparaten gelingt es ihren Verlauf, ihre Entstehungsstelle und ihre feine Struktur nachzuweisen.

Die amakrinen und horizontalen Zellen leben in vitro lange, fortschreitende Veränderungen lassen sich jedoch in ihnen nicht verfolgen. Das Zugrundegehen der Bipolaren wird sehr früh nachgewiesen. Die von Gliaelementen umgebenen Zellen leben verhältnissmässig lange. Gegen den 30-ten Tag des Lebens ausserhalb des Organismus beginnen sie zu degradieren. Ein Teil von ihnen kann in die Wachstumszone passiv verschleppt werden.

Besondere Veränderungen weisen die Müllerschen Fasern auf. Ihre apikalen Ende, welche die Mb. lim. ext. bilden, verkürzen sich, weshalb diese letzte zerstört wird. Die der Mb. lim. ext. anliegenden basalen Ende können abgerissen werden. Die Seitenfortsätze, mit deren Hilfe die Fasern in horizontaler Richtung in Verbindung standen, werden eingezogen und teils auch abgerissen. Der Kern wird heller und schwillt an. Der Körper nimmt eine zylindrische spindelförmige Gestalt an. Im Zytoplasma werden typische Gliafibrillen beobachtet, die sich gewöhnlich mit Mühe nachweisen lassen. Im Zusammenhang mit dem Zugrundegehen und der Auswanderung der Nervenelemente besteht die ganze innere Kernschicht auf diesen Stadien aus veränderten Müllerschen Elementen, die sich durch Mitose zu vermehren beginnen. Die sich teilenden Zellen der inneren Kernschicht unterscheiden sich wenig von den sich vermehrenden Elementen der äusseren Schicht. Die Auswanderung der Zellen der inneren Schicht kann auch in zwei Richtungen verlaufen—in der Richtung der Mb. lim. ext. und Mb. lim. int. Die sich vermehrenden Elemente beider Schichten wandern nicht immer in die Wachstumszone aus. Die Grenzen zwischen beiden Schichten gehen solchenfalls verloren und diese Bezirke erinnern sehr an die frühen Stadien der Embryogenese der Netzhaut. An der Stelle des Risses der Mb. lim. ext. sind die sich in die Wachstumszone verschiebenden Elemente der äusseren und inneren Schicht praktisch ununterscheidbar. Etwas beständiger ist die Struktur der Kerne in den Zellen, die genetisch aus der äusseren Netzhautschicht entstehen. Auf den späten Züchtungsstadien geht dieser Unterschied vollends verloren.

Im Falle eines langen Erhaltenbleibens der Mb. lim. ext. kann die Wucherung auch unter ihrer Decke vor sich gehen, wobei das Explantat sich in ein Knäulchen von einem sehr verwickelten Bau verwandelt. Im Zusammenhang mit der Verschiebung der meisten Elemente in die Wachstumszone verarmen die nicht wachsenden Bezirke, die sich in der Nachbarschaft der Stellen des intensiven Wachstums befinden, bedeutend an Zellen und werden locker. In einer solchen an Elementen verarmten Netzhaut gelang es in der inneren Kernschicht grosse lamelläre Zellen, anscheinend von Glianatur, nachzuweisen, die sich in bezug auf die Müllerschen Zellen senkrecht anordnen.

Die Wachstumselemente des perzeptorischen Blattes der Netzhaut unterliegen dem schon bekannten Verwandlungszyklus, welcher sich vollends mit den Bildern deckt, die vom Verfasser für den blinden Teil der Netzhaut und besonders für die Pigmentschicht des Sehblattes beschrieben wurden. Die Eigenartigkeit der Wachstumszone findet darin Ausdruck, dass hierneben allen möglichen wachsenden Komplexen—epithelartigen Membranen, Zügen und einzelnen Elementen—auch Nervenfasern angetroffen werden. Manche Eigentümlichkeiten werden auch im Assortiment der Chromosomen der sich teilenden Zellen beobachtet. Im Zytoplasma wird ein fibrillärer Bau nachgewiesen.

Ausserdem können die Elemente, deren Entstehen aus der äusseren Kernschicht sich kundtut, am 12—24-ten Tage nach der Explantation in der Wachstumszone lange, feine fadenförmige Protoplasmazüge bilden, die den Nervenfasern sehr ähnlich aussehen. Zuweilen werden in den lange nicht ausgeschnittenen Kulturen, in den Elementen der Wachstumszone Pigmentgranula nachgewiesen. Die Verwandlung und das Schicksal der Elemente der Wachstumszone des perzeptorischen Blattes, sowie anderer Bezirke des Augenbechers, verläuft in vitro nach dem Gliatypus, der an verschiedenen Objekten neuralen Ursprungs im Laboratorium von N. G. Chlopin (6) festgestellt wurde.

Die experimentelle Analyse der Histogenese der Netzhaut in Gewebekulturen macht es möglich die Prozesse, die in diesem Teile des Augenbechers vor sich gehen, näher zu verstehen. Die Ähnlichkeit des Pigmentblattes und des

perzeptorischen Blattes unter Explantationsbedingungen muss durch die gemeinsame histologische Determination und die Möglichkeit ihrer Verwandlung ineinander auf bestimmten Stadien der Ontogenese erklärt werden(5). Das geschilderte tatsächliche Material gestattet es, die Schlussfolgerung über die Bipotenz der kambialen Netzhautschicht zu ziehen, welche im Prozess der Ontogenese Elemente gibt, die sich zur neuronalen und glialen Seite entwickeln. Die dualistische Nature des restlichen embryonalen Kambiums, das sich in die Sehelemente verwandelt, kommt unter den Bedingungen des Experiments zum Ausdruck. Die Müllerschen Fasern in vitro werden von den proliferierenden Elementen der äusseren Kernschicht ununterscheidbar. Das Schicksal der Neuronen der Netzhaut ist ein ganz anderes. Sie können mit den Zellen der Stäbchen und Zapfen und den Müllerschen Fasern weder nach den funktionellen, noch nach den morphologischen Eigentümlichkeiten, die sich im Laufe ihrer phylogenetischen Entwicklung einprägen, verglichen werden.

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PALÉONTOLOGIE

NOTES SUR QUELQUES *PELMATOZOA* PERMIENS

Par N. YAKOVLEV, membre correspondant de l'Académie

I. Sur l'établissement d'un nouveau genre *Proindocrinus* Yakovl. J'ai décrit (1) du Permien inférieur de Krasnooufimsk dans l'Oural une forme que j'ai rapportée au genre *Indocrinus* Wanner, détermination que n'a pas contestée le prof. Wanner, qui l'a citée et qui a même rangé cette forme—*Indocrinus Piszowi*—dans un sous-groupe des nombreux *Indocrinus* de Timor décrits par lui (2). Nous nous sommes laissés entraîner par les traits de ressemblance (comme dans le cas de la détermination de *Timoroblastus Wanneri* Yakovl.), qui sautent aux yeux de prime abord, et n'avons pas aperçu une différence essentielle, à savoir le nombre des plaques anales, qui constitue en général un caractère important et de plus générique.

Wanner indique chez *Indocrinus* 3 analia. Je propose donc de considérer *Indocrinus Piszowi* comme le type d'un nouveau genre *Proindocrinus*, les relations entre les genres *Hemiindocrinus* Yakovl., *Proindocrinus* Yakovl. et *Indocrinus* Wanner se présentant comme suit:

Hemiindocrinus Yakovl.—5 bras, 3 analia, pas de fossettes aux angles des plaques du calice.

Proindocrinus Yakovl.—3 bras, 3 analia, présence de fossettes aux angles des plaques du calice.

Indocrinus Wanner—3 bras, 1—0 analia, présence de fossettes aux angles des plaques du calice.

Il existe donc dans l'Oural des genres *Hemiindocrinus* et *Proindocrinus* plus primitifs qu' *Indocrinus* ce qui est conforme à la supposition que j'ai plus d'une fois exprimée de l'âge plus ancien de la faune de Krasnooufimsk en comparaison avec celle de Timor.

II. Sur la trouvaille d'un blastoïde dans le Permien de la Sicile. Nous pouvons établir pour la première fois la présence d'un blastoïde dans la faune permienne de la Sicile. D'après deux échantillons, quoique incomplets, que m'a envoyés le professeur Stefanini (décédé en 1938), cette forme peut être déterminée comme *Schizoblastus* aff. *permicus* Wanner. La faune de Krasnooufimsk paraît ne renfermer, comme celle de la Sicile, qu'un seul blastoïde. Le blastoïde silicien se rapproche le plus d'un des blastoïdes les plus communs dans la faune de Timor, s'il ne lui est pas identique. Si un seul blastoïde de la faune de Timor a pu atteindre la Sicile, cela a dû être naturellement un de ceux qui possédaient la plus forte vitalité et qui par suite étaient les plus répandus.

III. Sur *Agassizocrinus* et *Petschoracrinus*. J'ai déjà étudié dans plusieurs Mémoires (3) le genre *Petschoracrinus*, établi par moi. Le travail de Harrell L. Strimple (6) montre que ce genre se rencontre non seulement en

URSS, mais aussi dans l'Amérique du Nord. Strimple décrit une nouvelle espèce d'*Agassizocrinus* (*A. tarri*) présentant précisément le caractère qui distingue le genre *Petschoracrinus*—une seule plaque anale ne dépassant pas en haut la couronne des *RR* et ayant une forme trapézoïdale retrécie vers le haut. Il convient d'observer que le genre *Agassizocrinus* Owen et Shumard se caractérise par la présence de 3 analia. Nous en trouvons l'indication chez Bather ([4]), chez Zittel ([7]) et aussi dans un récent travail de Moore et Plummer([5]).

Moore et Plummer signalent que des 17 espèces d'*Agassizocrinus* décrites, toutes sauf une se rencontrent dans le Carbonifère inférieur (Mississipian, Chester group); l'exception concernant la présence dans le lower et middle Pennsylvanian de l'Arkansas, de l'Oklahoma, du Kansas et du Texas se rapporte peut-être à des formes dans le genre de *A. tarri*, qui a été trouvé dans le Pennsylvanian de l'Oklahoma.

Agassizocrinus et *Petschoracrinus* se ressemblent par la réduction de la tige et l'épaissement des plaques du calice, résultat de la vie dans la zone littorale, masi il se peut même que le premier ne soit pas l'ancêtre du second, car la réduction de la tige y est plus avancée que chez le dernier, allant jusqu'à l'atrophie. En outre, on constate assez souvent chez *Agassizocrinus* une oblitération des sutures entre les plaques de la base, qui n'existe pas chez *Petschoracrinus* ou y présente un autre caractère. La perte de la fixation par la tige et l'épaississement des parois du calice sont dus évidemment à la vie dans la zone littorale à diverses périodes, et les formes qui ont perdu la fixation ne dérivent pas directement les unes des autres, mais ont chaque fois un autre ancêtre muni d'une tige.

Tout cela, et en particulier la présence d'une seule plaque anale, nous autorise à considérer *Petschoracrinus* comme un genre autonome, qui se rencontre dans le Permien et le Carbonifère supérieur.

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PALEONTOLOGY

FIRST REPRESENTATIVE OF THE GENUS *PARASHUMARDITES* FROM THE UPPER CARBONIFEROUS OF MOSCOW

By V. E. RUZHENCEV

(Communicated by A. A. Borissiak, Member of the Academy, 11. VII. 1939)

In the author's previous communication(3)a new genus *Parashumardites* has been established. After some time, a young naturalist, V. Bezobrazov, handed to E. A. Ivanova an ammonite found by him in the limestone waste of the Moscow subway. Ivanova kindly presented this interesting form to the author for investigation. We lack exact information as to the locality where the mentioned ammonite comes from. It can only be asserted that the waste was derived from the tunnel of the Pokrovsky radius, i. e., the ammonite-bearing dolomite was most likely found somewhere near the Kursky station. Basing upon the generalized section of Moscow, we can maintain that the form at hand is to be referred to one of the middle members of the Teguliferina beds. The description of this ammonite may be important from various points of view: it is the first representative of the genus *Parashumardites* in the Upper Carboniferous of the Moscow basin and of the USSR on the whole; besides, it is a representative of such a genus which seems to be suitable for interregional correlation. The study of the specimen led the author to a conclusion that it belongs to a new species, to which the following name is assigned:

Parashumardites mosquensis sp. nov.

Shape. The only specimen is rather poorly preserved. In Fig. 1 is shown the shape of the conch restored after a thorough study and measurement of the fragment. Solid lines stand for the portions of the conch which can be seen on the fragment itself.

Form subglobose with volutions helmet-shaped in cross-section, wider than high. The lateral and ventral sides form a regularly rounded surface. The umbilical shoulder smooth, unprominent. The umbilical wall rounded and not very steep. The umbilicus middle-sized and stepped.

Sculpture is unknown, since the specimen represents the internal mold which is quite smooth.

Suture (Fig. 1, *C* and *D*) consists of twelve main lobes and as many saddles. The ventral lobe is divided by a ventral saddle into two branches. The ventral saddle is not very high, bottle-shaped and notched at the top. The branches of the ventral lobe are curved terminally towards the siphon; they are asymmetrical, acuminate, their siphonal sides being especially prominent. The first lateral saddle is high, relatively broad, but very constricted in the middle, and somewhat asymmetrical, its rather rounded summit being

more prominent umbilically. The first lateral lobe is exceedingly broad, divided into three branches by two rather high additional saddles rounded at the top. Two outside branches are short, rounded at the base and similarly though inversely outlined. The middle branch is long, very acuminate, and rather lanceolate. The inner additional saddle of the first lobe is somewhat higher and by far broader than the outer one. The second lateral saddle is smaller than the first one and is inversely outlined. The second lateral lobe is small, entire, basally rounded. The next asymmetrical lateral saddle located near the umbilical shoulder connects the preceding lobe with the umbilical one. The latter is wedge-shaped and is closer to the umbilical shoulder than to the seam. The umbilical saddle located partly on the internal side of the conch is rather broad, with flat but somewhat ripply summit.

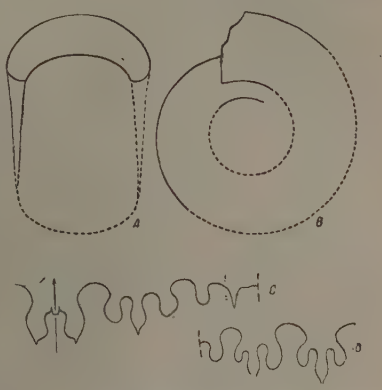

Fig. 1. *Parashumardites mosquensis* sp. nov. ($\times 1/2$). *A*, *B*—ventral and lateral outlines; *C*—external suture at $H=14.0$ mm; *D*—internal suture at $H=20.0$ mm. Teguliferina beds, Moscow.

The dorsal lobe is moderately broad and sharply trifid, at the upper part very constricted. The side prongs of the lobe are rounded and curved, while the middle one, being much longer, is acuminate. The first internal lateral saddle is very constricted at the base and broadly rounded at the top. The first internal lateral lobe is also trifid but quite asymmetrically outlined. Its outside prongs have the same though inverse shape, but they are different in size, the inner prong, i. e., the one directed towards the umbilicus, being much smaller than the outer one. The middle prong is on the whole spear-like, and is much longer than the adjacent prongs. As the inner additional saddle is by far smaller, the middle prong is located quite asymmetrically in relation to the whole lobe. The second internal lateral saddle is constricted in the lower portion and rounded at the summit. The second internal lateral lobe is small, entire, basally rounded, and somewhat curved towards the umbilicus.

Dimensions:	*D*	*H*	*W*	*Du*	*H*:*D*	*W*:*D*	*Du*:*D*	*H*:*W*
	65.0	20.2	42.8	27.8(?)	0.31	0.66	0.43	0.47

Since the conch is rather poorly preserved, the above data cannot be regarded as perfectly accurate, yet, in the author's opinion, they are close to that. The mature individuals of the species might be very large, which is evident from the fact that the specimen at our disposal, at the diameter of 65.0 mm, is formed throughout the whole conch by air chambers.

Relation to Other Species. The representatives of this genus have so far been known from the Upper Carboniferous of the United States only. The following species were established there: *Parashumardites senex* M. et C. (genotype), *P. cuyleri* P. et S., *P. fornicatus* P. et S., and *P. sellardsi* P. et S. Our species is distinguished from all the above-mentioned American representatives.

In comparison with *P. senex* the species in question has the following distinctions. The branches of the ventral lobe are not so drawn out and are less acuminate. The first lateral lobe is asymmetrical, since its inner additional saddle is by far broader than the outer one, while in *P. senex* the corresponding lobe is nearly quite symmetrical. The dorsal lobe in our case is more diffe-

rentiated, and the second internal lateral lobe is less broad. In the shape of the conch some dissimilarities can also be observed. The above-stated differences between *P. mosquensis* and *P. senex* are observed in the case of *P. sellardsi* as well. The latter is, however, poorly preserved, which prevents a more detailed comparison.

The distinction from two other American species is still more obvious. We can, for example, note that in *P. fornicatus* the ventral lobe is by far shorter than in *P. mosquensis*. As to *P. cuyleri*, it shows such sutures, particularly on the internal side, the outline of which is completely different from that of *P. mosquensis*.

Locality. The limestone waste, Semenovskaia quay, Moscow.

Remarks. To summarize briefly the results of the above study we can state that the discovery of *Parashumardites mosquensis* in the Upper Carboniferous of the Moscow basin seems to be a fact of great interest. *Parashumardites* is a genus of closely related species which have up to now been found solely in the Upper Carboniferous of North America. *P. senex* comes from the Nellie Bly formation, a member of the Kansas City group. This formation is believed by Miller and Cline(1) to be equivalent to the Palo Pinto limestone of north-central Texas. The Palo Pinto limestone occurs at the base of the Canyon group, i. e. at the base of the Upper Carboniferous in our interpretation. *P. fornicatus* has been collected in the Graford formation, Canyon group, just above the Palo Pinto limestone. *P. sellardsi* has been found in the Marathon area of west Texas, in the Lower Gaptank formation, i. e. in the beds which must be equivalent to the Canyon group. Finally, *P. cuyleri* comes from beds, occurring near the base of the Graham formation, the lowermost member of the Cisco group(2). In view of what has been quoted, it becomes clear that all the known American species have been encountered in the lower portion of the Upper Carboniferous.

It remains to consider the significance of the discovery of *Parashumardites mosquensis* in the Teguliferina beds of Moscow. This stratigraphic level has so far been devoid of ammonites. The above-described species, according to the data of Ivanova, has been collected together with such typical Upper Carboniferous brachiopods as *Buxtonia subpunctata* Nik., *Linoproductus lineatus* Waag. and *L. cora* Orb. var. *tschernyschewi* Ivan. *Parashumardites mosquensis* is a form closely related to the American species, in particular, to *P. senex* and *P. sellardsi*. The stage of development and the similarity of the faunas compared indicate that the Teguliferina beds of the Moscow basin are not essentially different in age from the Canyon group of the North America sequence. This fact may emphasize the superiority of ammonites as index fossils for stratigraphic correlation, especially for the interregional one. More convincing criteria may hardly be found.

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PALEONTOLOGY

TWO NEW SPECIES OF THE GENUS *PROPINACOCERAS* GEMMELLARO

By V. E. RUZHENCEV

(Communicated by A. A. Borissiak, Member of the Academy, 6. VII. 1939)

Representatives of the genus *Propinacoceras* are very rare in the Permian deposits of the Urals. Karpinsky described a species named by him *P. sakmarae;* yet, its suture was studied very incompletely, the specimens being rather poorly preserved. Maximova has recently established a new species, *P. ajense*, which comes from Aj river, Bashkiria. The former was collected in the Sakmarian, while the latter is known to occur in the Artinskian. Our knowledge of the Uralian *Propinacoceras* was exhausted by the two above-mentioned species. From the above-said it is clear that the discovery of two new species deserves more than ordinary interest. The fossils described below have been collected by the author in the Artinskian. They come from two localitites: Aktasty river and Jil-tau mount, both in the Aktjubinsk region, South Urals.

Propinacoceras rhipaeum sp. nov. (Fig. 1, *a*—*e*)

S h a p e. Conch discoidal, completely involute. A quite broad lateral side is somewhat convex in the mid-portion (closer to the umbilicus), and considerably concave in the proximity to the passage to the external side. Ventral border rounded. The umbilical shoulder not prominent. The ventral side consists of three parts: two broad rows of tubercles and a deep narrow furrow. Umbilicus completely closed.

S c u l p t u r e. The lateral sides of the conch are marked by delicate transverse striae. Throughout the umbilical half of the lateral side they are very fine and form a swing backwards. On the second half they become more distinct, are more widely spaced, and run almost linearly, forming a weak sinus within the concave zone. Thus, in the mid-portion of the lateral side, all striae form a characteristic flexure-like bend. The ventral side is ornamented with two rows of tubercles regularly rounded in adolescent forms and becoming transversely oblong in the adult. They are prominent on the ventral side, just slightly pronounced in the bordering zone of the lateral side, while they do not extend to the concave zone. The number of tubercles on the volution attains 47 at a conch diameter of 22 mm, this number increasing but slightly with growth.

S u t u r e. The ventral lobe is long, rather broad, somewhat constricted at the top and trifid at the base. A very broad saddle is present between the ventral and the first lateral lobes. It is complicated by adventitious lobes at the summit and on the inner side. One of them, located at the summit,

is highly variable in its outlines. In typical forms it is broad and subdivided into two equally large pointed parts. In a number of cases, however, these parts may be rounded, disproportionate in length and width, the whole lobe becoming asymmetrically outlined. The lateral adventitious lobe is long, narrow, slightly constricted at the top, and distinctly bifid. The first lateral lobe is long, narrow, asymmetrical, and bifid. Its base is much lower in posi-

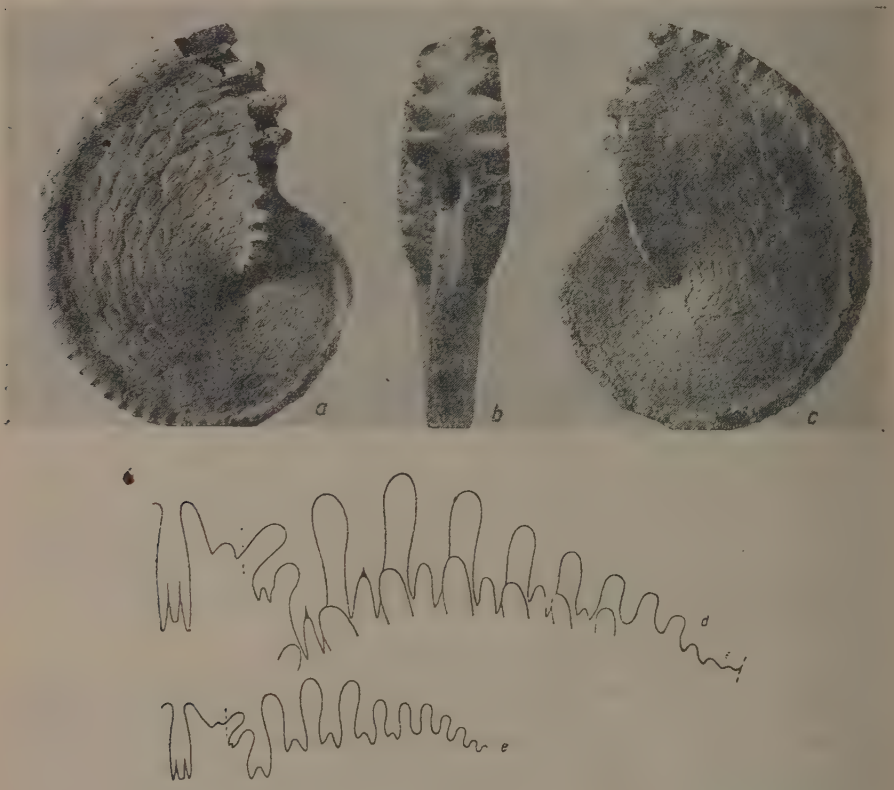

Fig. 1. *Propinacoceras rhipaeum* sp. nov.: *a*, *b*, *c*—three views of the holotype (×1); *d*—suture of the same specimen at H=36.0 mm (×2); *e*—suture of an adolescent conch at H=12.5 mm (×3.3). Aktasty river. Artinskian.

tion than that of the ventral lobe. The second lateral lobe is also fairly bifid, its base being much higher than that of the preceding lobe. The following four lobes, which gradually diminish in size towards the umbilicus, are bifid. The lateral lobes, from the seventh to the tenth inclusive, are entire. On the umbilical shoulder one more weakly developed lobe is present. Another incipient lobe adjoins the umbilical seam. Thus, in adult specimens ten lateral lobes and two umbilical ones are present. The first six lateral lobes are bifid. Because of the close spacing of the septa, no less than five lateral lobes are in contact with the preceding suture.

Dimensions:		D	H	W	$H:D$	$W:D$
(holotype)	I	60.0	37.5	15.0	0.63	0.25
	II	22.0	14.0	5.0	0.64	0.23

Relation to Other Species. *Propinacoceras rhipaeum* is a highly peculiar form greatly different from all representatives of the genus, particularly by its first lateral lobe being much lower when compared with the next one.

Locality. The above species abounds in the lower dolomite ridge of Aktasty river. Three specimens have been found in the dolomite of Jil-tau mount, Jaksy-Kargala river.

Propinacoceras aktubense sp. nov. (Fig. 2, *a*—*g*)

Shape. Conch discoidal, with flat parallel sides, flattened ventral side, and almost closed umbilicus. The passage from the lateral to the umbi-

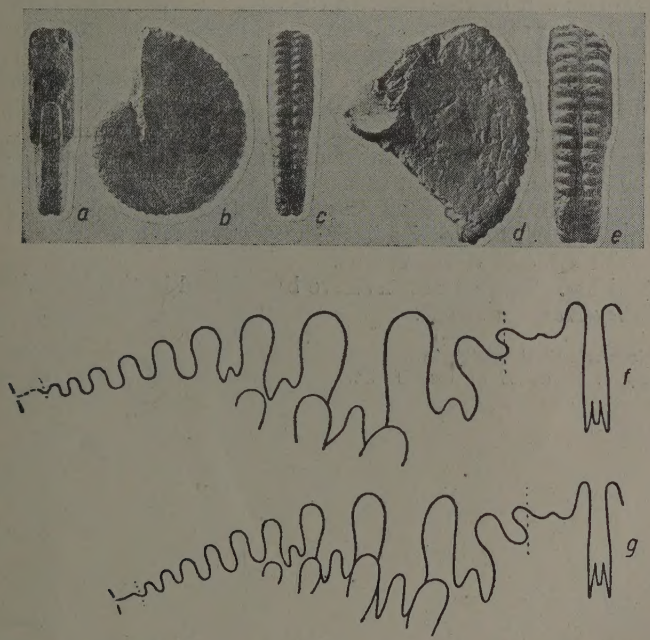

Fig. 2. *Propinacoceras aktubense* sp. nov.: *a*, *b*, *c*—three views of the holotype (× 1); *d*, *e*—two views of the second specimen (× 1); *f*—suture of the holotype at $H=15.0$ mm (× 5); *g*—sutpyre of the second specimen at $H=20.0$ mm (× 3). Jil-tau mount. Artinskian.

lical and ventral sides rounded. The ventral side made up of three parts: two broad rows of tubercles and a deep separating furrow, half as wide.

Sculpture. The test layer has not been preserved, but in the mold tubercles are quite distinct. In young specimens they are circular in outline, while in the adult they become oblong, remaining strictly opposite throughout the entire growth period. The side of each tubercle facing the siphon is more abrupt than the opposite one. Tubercles are not continuous on the lateral wall. At a diameter of 26.7 mm there are 27 tubercles on the half-volution of the holotype. On the quarter-volution of the second specimen, at the average height of 19.0 mm, there are 18 tubercles.

Suture is shown in Fig. 2, *f*,*g*. The external saddle is very wide and complicated by two adventitious lobes. The outer one is broad and subdivided. The inner one is narrow, entire, disposed somewhat obliquely. There

are ten lateral lobes altogether. Only four of them are bifid, the remaining being entire. The second lateral lobe is the largest one, its termination being much lower than that of the two adjoining lobes. Because of the close spacing of the septa, the second and third lateral lobes deeply penetrate into the preceding suture.

Dimensions:		*D*	*H*	*W*	*H* : *D*	*W* : *D*
	I	—	22.3	8.6	—	—
(holotype)	II	26.7	15.7	6.7	0.59	0.25

Relation to Other Species. The above species exhibits greatest similarity to *Propinacoceras ajense* Max. The shape of the conch in two cases is approximately the same, though upon detailed comparison a number of differences can be observed. In the first place, a fact fixes one's attention that in *P. ajense* the height of the whorl is somewhat greater, the width, on the contrary, being less. As a result, the conch disc of the Aktjubinsk species turns out to be thicker than in *P. ajense*, their diameters being equal. The next difference is that the lateral sides of our species are parallel, while in *P. ajense* they somewhat converge umbilically. The sutures of the two species compared have the same number of lobes. But our species, at a height of the whorl of about 20.0 mm, shows only four bifid lateral lobes, the fifth being basally quite rounded, whereas in *P. ajense* six or even more lateral lobes are bifid. Thus, the species from the Aj river seems to be at a somewhat more advanced stage of development.

Locality. Two specimens have been found in the dolomite of Jil-tau mount, Jaksy-Kargala river.

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